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OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVIII AUGUST 1953 No. 8

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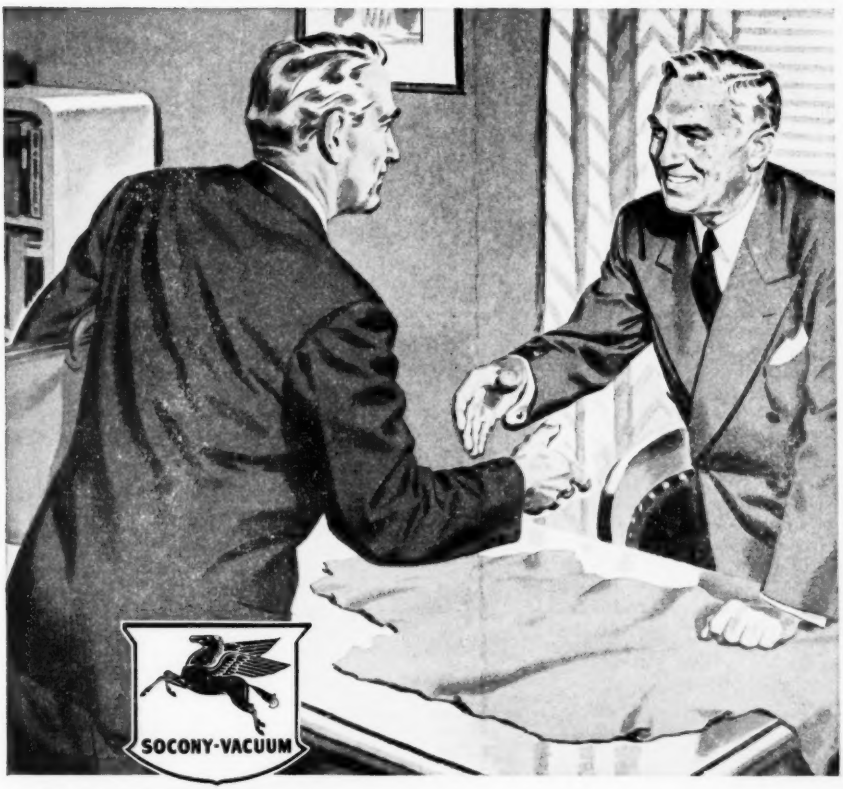

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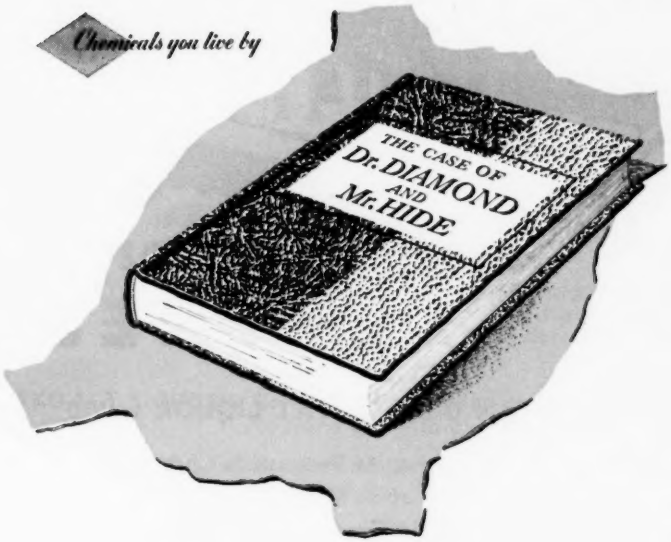

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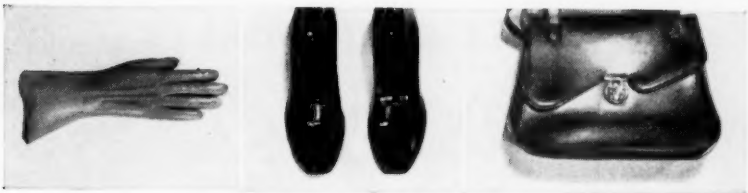

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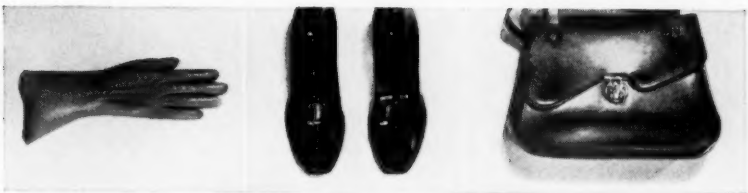

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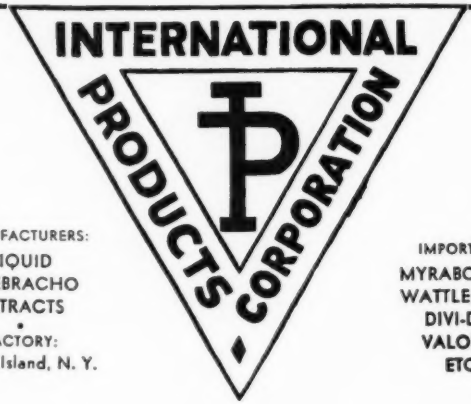

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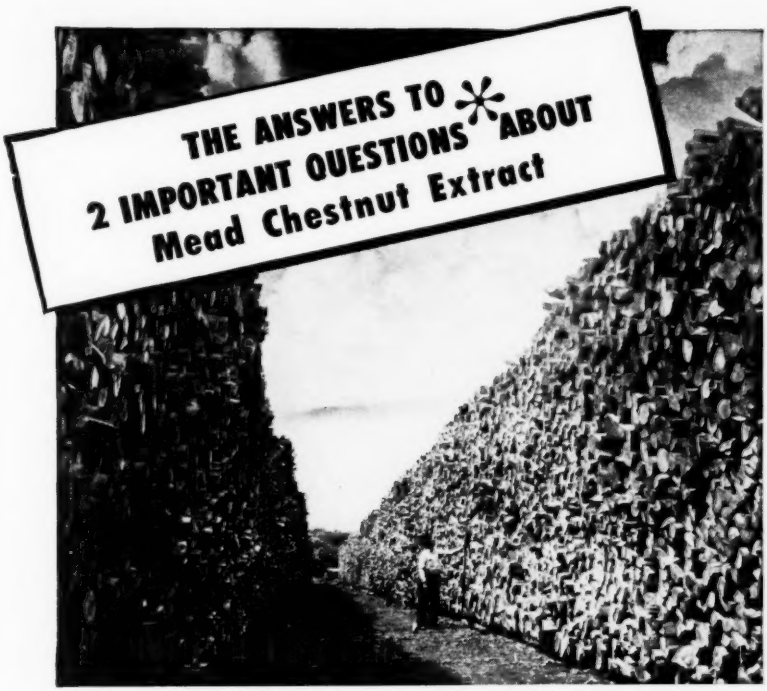

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Tanning Material A	61%
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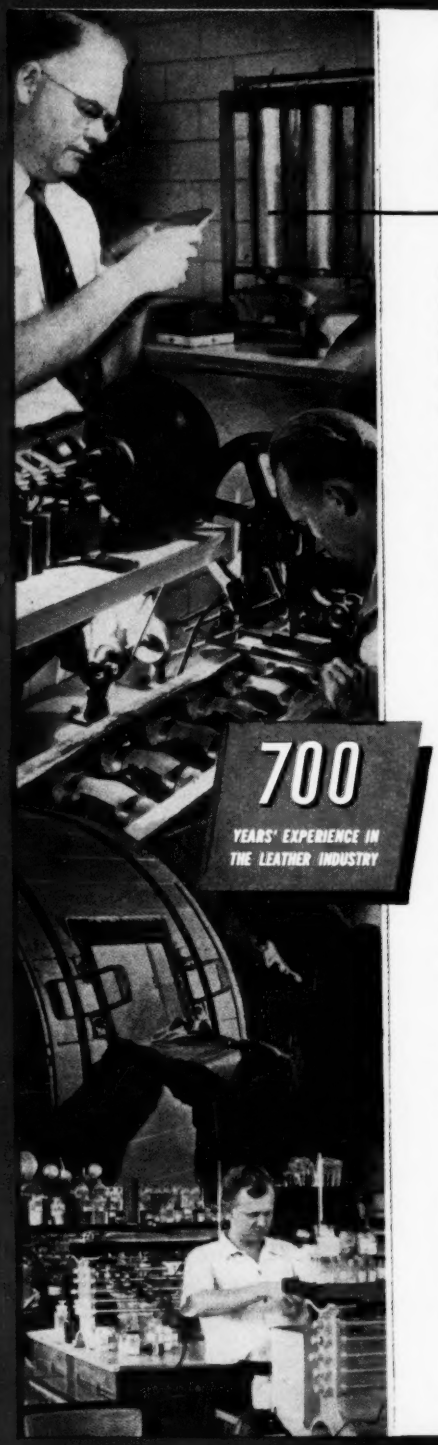

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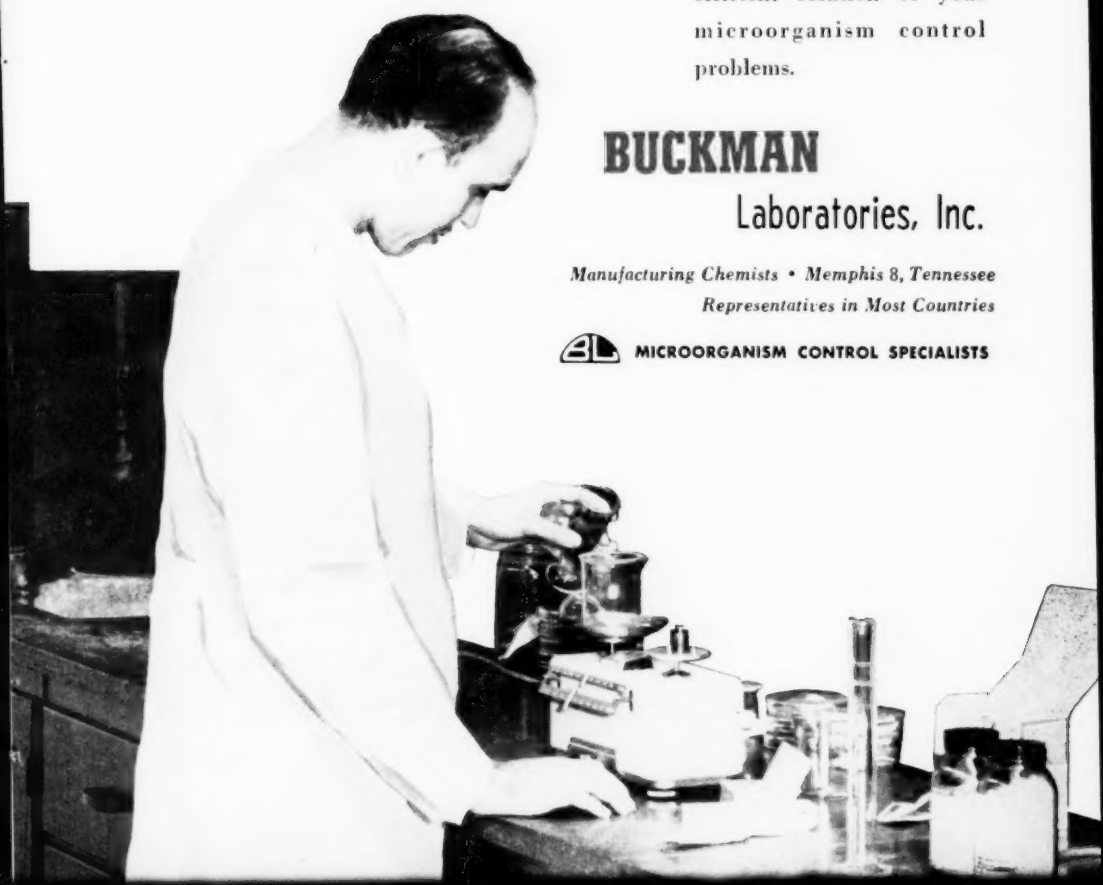

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ANALYSIS

Na_2S	60 to 62%
NaCl	1.5% Max.
Other Na Salts	2.0% Max.
Fe	8 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	35% Min.

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Mol. Wt. 56.1
M.P. . . . . 55°C

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Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
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VOL. XLVIII AUGUST 1953 No. 8

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EDWIN RAYMOND THEIS

The morning of April 25, 1953, brought to an end a remarkable career.

Professor Edwin Raymond Theis was born in Newport, Kentucky, July 8, 1896. He served as an infantry officer in 1918 and as a reserve officer until his death. After the War he attended the University of Cincinnati, from which he graduated in 1921, winning the Hockstetter prize for original scientific research. He stayed on at Cincinnati as Associate Director of the Tanners' Research Laboratory and in 1926 was granted a Ph.D. degree in biochemistry. After a year of pharmaceutical research at Ames, Iowa, and at Detroit he joined the faculty of Lehigh University as Assistant Professor of Chemical Engineering. At Lehigh he was advanced to Professor in 1938 and in 1945 was apointed Director of the Division of Leather Technology, a post he filled until his death at the age of 57.

He leaves behind him an international reputation for technical competence and for service to man. In 1937 he went to China on a Government mission in connection with imported furs. While in the Orient he gathered information on primitive tanning processes. In 1946 he was invited to England to lecture before the Society of International Leather Trades Chemists at London and before the Faraday Society, honors which his many friends in the ALCA recognized with a testimonal dinner at the Hotel Pennsylvania. In 1951 he again went abroad, this time at invitation of the Dutch Government and of the Economic Cooperation Administration, to address tanners and leather chemists of the Netherlands. This international reputation as an authority on chrome tanning and other phases of leather manufacture was based upon his many research publications and his wide experience as consultant both to the leather industry and to the United States Government. He was co-author, with the late George D. McLaughlin, of *The Chemistry of Leather Manufacture* published in 1945, was a member of the American Chemical Society, Tau Beta Pi, Sigma Xi, Delta Sigma Phi, and a Fellow of the American Institute of Chemists. In 1943 he was awarded the Fraser Muir Moffett Medal by the Tanners' Council of America and in 1947 a Life Membership in the ALCA.

The core of his life's work was—indeed still is—at Lehigh University. There he worked for twenty-five years, writing his many research articles; from there he visited tanneries, observing, talking with men in the leather industry, returning to his laboratory to test out new ideas or to reexamine the old. The Lehigh University Leather Technology Laboratory he built to a position of excellence recognized even beyond this country. During his eight years as its Director, Dr. Theis supervised a special research program designed to develop the practical applications of the products of research. In this program his energies and scientific imagination benefitted the leather industry, notably in developing new techniques for chrome tanning.

As tangible monuments to Professor Theis are the Lehigh Laboratory and the vast number of published studies that bear his name. But just as import-

ant is his intangible monument; the influence he had upon the young scientists he trained in scientific curiosity, in thoroughness, and in hard work, and who learned from him of the challenging mysteries that lie below the surface of an ordinary piece of leather. They will remember him always. And so will his many friends, both in the leather industry and out of it, who know his work and what he lived for. His impression upon all of these has been strong; and the interest he stimulated in leather research continues in the work going forward both here and abroad. But though his work goes on, Dr. Theis can never be "replaced". He can just be missed.

Dr. Theis is survived by his wife, Martha Pauling Theis, his father, two sons, and a brother. To them we extend our deepest sympathy and mourn with them in their loss. Memorial services for Dr. Edwin Raymond Theis were held April 28, 1953, in Packer Memorial Church on the Lehigh Campus.

EDWIN B. THORSTENSEN.

BARCELONA MEETING OF THE INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

The Union announces that its meeting will be held from the thirteenth to the eighteenth of next September, thus reverting to the original date announced in the Journal.

REQUEST FOR A.L.C.A. SAMPLING METHODS BOOKLETS

The School of Leather and Tanning Technology of Pratt Institute is in need of copies of the Association Methods of Sampling and Analysis. These methods booklets are used by the leather students at Pratt. The Institute will therefore appreciate receipt of any duplicate methods booklets which can be spared by members of the association.

Council Meeting Minutes
The American Leather Chemists Association

June 9, 1953
Netherland Plaza
Cincinnati, Ohio

A meeting of Council was held at 10:30 A. M. on this day. Present were President Turley, President-Elect Flinn, Council Members Collins, Hobbs, Morrison, Ross and Windus; also Messers. Kirk, Meo, Hague, Williams and O'Flaherty.

The minutes of the last meeting on February 12th were given final approval.

Dr. Flinn reported that he had a meeting of the coordinating committee (this is made up of the chairmen of all technical committees.) Each committee will render a report on the status of their work present and future. Dr. Flinn will resume' these reports and publish same.

Council approved the mail vote to make all past presidents Life Members.

Editor Dean Williams reported that the publication of the symposium record of the New England Production Club from last year's annual meeting was now at the printers.

Dr. Kirk reported briefly on the convention, a final report will be made at the next Council meeting. He reported he had dates available at Bedford Springs. He had visited the place and found it in fine condition and capable of handling a meeting of our size. Council approved Bedford Springs as the place and accepted the dates, June 7–10, unless it is possible to get dates late in May. Dr. Kirk is to determine this.

Mr. Meo reported briefly on the entertainment situation and reported that the golf prizes would be distributed Wednesday evening, June 10th., at the registration desk.

Mr. Hague reported on publicity and that he had kept within his budget.

President Turley appointed Messrs. Whitmore, Bundy, and Thorstensen, chairman, to be the auditors and count the ballots. Mr. Thayer served in Mr. Bundy's place as Mr. Bundy was not available at the time of the count.

The auditors reported the following candidates elected as members of Council.

R. Henrich
J. Kanagy
H. Wilson

Mr. Teas reported for the Ways and Means Committee that it appeared there would be a deficit with the meeting. Upon motion of Mr. Morrison, seconded by Dr. Windus, and unanimously approved by Council, it was agreed that all money in the Convention Committee treasury plus all money received from registration and ticket sales should be used to pay the expenses and then pay the difference from the regular treasury.

It was then agreed that the new Council should consider making an advance to the Convention Committee treasury.

President Turley with final approval of Council made the following appointments as the Nominating Committee.

V. Mlejnek
B. W. Crago
R. Nelson, chairman

The meeting adjourned at 12:00 noon with the thought that another Council meeting with the newly elected Council members would be held later during the annual meeting.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary.*

Council Meeting Minutes
The American Leather Chemists Association

June 10, 1953
Tanners' Research Laboratory
Cincinnati, Ohio

A meeting of Council was held at 3:45 P. M. Present were President Turley, President-Elect Flinn, Council Members Collins, Henrich, Ross, and Wilson; also Messrs. Williams and O'Flaherty.

Dr. Turley explained that there would be a deficit from the meeting expenses and that Council had yesterday agreed to pay the deficit from general funds. This was approved by the present Council.

Dr. Turley reported that Bedford Springs has been selected for the 1954 meeting site with the dates of June 7–10th.

Council was informed of the 1953–1954 Nominating Committee and approved it. The Secretary is to advise the committee that it is the feeling of Council that the candidates for President-Elect shall be persons actively engaged in the leather industry.

The following members, each fulfilling the requirements were elected to active membership—

Mr. F. Paul Cronin
Mr. Henry L. Fober
Mr. Bernard F. Judd
Mr. James K. Koeniger
Mr. John F. Lyons, Jr.
Mr. Maurice Marcotte
Mr. Robert E. Merritt
Mr. Richard G. Moulton
Mr. Anthony J. Pilar, Jr.
Mr. Paul C. Stahnke
Mr. R. Lee Southwood

The next Council meeting was agreed to be held at Cincinnati, Ohio on November 10, 1953.

The meeting adjourned at 4:24 P. M.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary.*

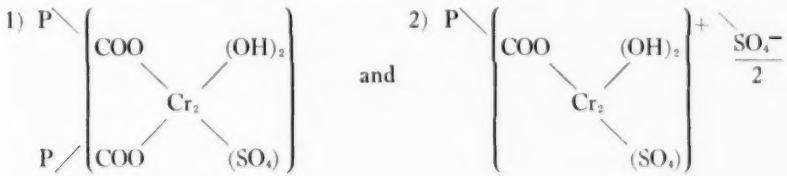
Remarks on Isoelectric Points of Chromed Collagen

By K. H. GUSTAVSON

In a recent note, with July 20, 1952 as the date of receipt, Shuttleworth and Cunningham [1] commenting on the author's paper [2] on "The iso-electric Points of Chromium Collagen Compounds" published in the Journal of *June*, 1952, state that the isoelectric point (I.E.P.) may be raised or lowered according to the nature of the initial mean charge on the chrome complexes and that the direction of the shift cannot be taken to indicate whether acidic or basic protein groups are involved in the chrome tannage. As to the main findings, there is no disagreement.

It is apparent that, had the above authors not overlooked the cardinal points of the type of pretreatment given the chromed specimens of collagen before determination of the I.E.P. by the physical and chemical methods applied, as will be shown, no doubt much of their criticism of the paper in question would have been avoided. It should also be pointed out that in all circumstances, no matter what the premisses are, the algebraic complication of a rather simple case, as demonstrated by the authors, is not applicable to the systems discussed, since several quantities in the simple equations involved are not known and part of the reasoning is based on assumptions.

The problem resolves itself into this question. Tanning of collagen by basic chromium sulfates may be conceived to consist of the combination of polyvalent polynuclear chromium cations with collagen through its carboxyl ions. According to the availability of the carboxyl groups of collagen in its lattice and the steric conditions, the cationic chromium complexes may be either completely or only partially discharged by the carboxyl ions which penetrate into the internal sphere for direct co-ordination with chromium. Taking as an example, the sulfato-hydroxo-chromium complexes of 33 per cent acidity, represented by the empirical formula: $[Cr_2(OH)_2(SO_4)]^{2+}$, this complex may exist in combination with collagen as a bifunctionally reacting complex with *zero net charge* or as a unifunctional complex with *one positive charge*, which is balanced by one equivalent of ionic sulfate. In the first instance, two carboxyls have been acted upon by each complex, and in the second case only one carboxyl group has been introduced into the complex. The schematic formula may then be represented as:



omitting in both instances the aquo groups for completing the coordination number of chromium. Besides the ionic sulfate present as "Gegenion" (compensating ion) in 2), the chromed collagen contains sulfate ions associated with its cationic groups.

The case treated by Shuttleworth and Cunningham is represented by the unifunctional complex in example 2). Chrome-tanned collagen, containing the compound formed in this instance (No. 2), would not be suitable for use, as it is, in an electrophoretic determination, using solutions of buffers of low ionic strength (avoiding complexing anions in the buffer), since the effect of the residual charge of the attached chromium complex is an unknown quantity. It is to be noted, that being the cardinal point overlooked by the authors, which has repeatedly been stressed in my paper, that the specimens of chromed collagen, which were the object of the physico-chemical and chemical investigations for detecting and estimating the shift of the I.E.P. of collagen caused by the binding of cationic chromium complexes, were pretreated in 4 per cent pyridine solution for removal of ionic sulfate. It was especially pointed out that previous workers [3,4] had failed to comply with that requirement. Table I (p. 429) of my article gives the per cent acidity of the sulfato chromium complexes of the tanned specimens, the figures being 32 – 35 per cent. Moreover, it is expressly stated: "The average composition of the sulfato-chromium complexes fixed by collagen corresponds to the empirical formula: ($>Cr_2O.SO_4$)". Hence, by the alkaline pretreatment both the protein bound acid and the ionic sulfate compensating the unifunctional chromium complexes fixed by collagen (example 2) were removed. The positive charge of the unifunctional complex is nullified, since the hydroxyl group introduced during the pyridine treatment takes the place of the ionic sulfate, and enters into the chromium complex. However, this change will probably not contribute to the stabilization of the structure, since the final result will be, schematically pictured:

$$P - \left\{ \begin{array}{l} \\ COO.-Cr_2 \\ \\ \end{array} \begin{array}{l} (OH)_2 \\ \diagup \\ \\ \diagdown \\ SO_4 \end{array} \right\}$$

. The specimens studied in the author's investigation contained their chromium complexes in the form of the types given, *i.e., without electrical charge.* Hence, the shift in I.E.P. found, care being taken to eliminate secondary complications by complexing buffer ions and drying of the stock, proves beyond doubt the type of protein groups involved in the irreversible fixation of chromium complexes in the chrome tannage as regards their sign of charge. The close agreement of the results from the electrophoretic and electrokinetic methods, on one hand, and those obtained by the chemical technique (dyestuffs), on the other hand, appears to be

additional evidence for the reliability of the electro-potential methods under the experimental conditions applied in the cited investigation. Obviously, the deductions of Shuttleworth and Cunningham and their comments are irrelevant to the findings reported in the original paper.

In a separate paper [5], experimental data of a direct bearing on the problem of the uni-and multifunctional reactions of chromium complexes with collagen will be presented. These experiments concern the determination of the binding of chromium complexes in dilute gelatin solutions, the uncombined chromium being removed by means of ion exchangers. It has been found that the main part of the basic chromium salts behave towards gelatin as *unifunctional* agents. Similar conditions, although less pronounced, apply to the chroming of collagen. This has been indicated by data on the mean charge of the cationic chromium complexes present in solution obtained by means of ion exchange, with due consideration for the amounts of chromium fixed by collagen. These findings have been combined with data from approximation of the equivalent of carboxyl groups of collagen partaking in the binding of the chromium complexes.

Since no method for determination of free carboxyl groups in chrome tanned collagen is known, the proportion of the charged and uncharged chromium complexes in their attachment to collagen can only be roughly approximated. That is also one of the main reasons for the shortcomings of the derivations given by Shuttleworth and Cunningham.

The problem of *uni-* and *multi-functional* reactivity of chromium complexes towards collagen is particularly well illustrated by the 67 per cent acid chromium chloride, containing cationic hydroxo-chromium complexes solely. The tetravalent type may serve for characterization of the possibilities: $(Cr_2(OH)_2)^{4+}$. Thus, gelatin in one per cent solution treated with a large excess of the 67 per cent acid chromium chloride (about 25 per cent Cr_2O_3 on the weight of gelatin) will mainly combine with the cation $(Cr_2(OH)_2)Cl_2^+$.

The experimental demonstration of the shift of the I.E.P. of collagen towards higher pH values caused by its combination with cationic chromium salts (inactivation of carboxylic groups of collagen) given in my paper, has very recently been substantiated by data on the effect of chroming of vegetable proteins on the I.E.P. estimated by a third, independent physico-chemical technique. Thus, Petri and Staverman have studied the problem in a paper on "The Electrochemical Properties of Lupin Seed Protein" [6], presented in August 1952 at the Faraday Society Symposium on the Physical Chemistry of Proteins, Cambridge, England. Membranes of lupin seed protein were prepared and tanned with chromium sulfates. The membranes were characterized electrochemically by measuring the dialysis potential between KCl solution of 0.1 and 0.01 *N*, the membrane separating the cells, which were adjusted to various pH values. Graphically the zero potential was ascertained and designated as the I.E.P. The Dutch investigators found that,

by tanning the protein membrane with 5 per cent chrome alum on the weight of protein for instance, the I.E.P. was displaced up to pH values of 11 from the original I.E.P. of the untreated protein of pH 5. The apparatus used by Petri and Staverman, which now is in use in this Laboratory, has proven suitable for determination of the electrical potential of leather of various tannages, which forms a natural membrane, preferably in the form of a split with the grain and flesh layers removed. Details of the construction and the working of this apparatus with some typical results will be given in a forthcoming paper in another place.

During the course of thirty years, the present author has persistently maintained the view that the carboxyl ion of collagen is the group governing the fixation of cationic chromium complexes in spite of strong opposition from some prominent investigators during the twenties and thirties. In view of the recent accentuation of the "discovery" of the predominating function of the carboxyl ions of collagen for the binding of chromium compounds by collagen[7], it seems opportune to remind of the fact that the promulgation of the concept of the interaction of cationic chromium complexes with the carboxyl ions of collagen, in solutions of pH values lower than the I.E.P. of collagen, was the logical outcome of applying the ampho-ionic ("Zwitter"-ion) concept to this reaction. This was done in 1925[8], the year after the appearance of Bjerrrum's classical paper. In the final analysis, the original idea of the governing function of the carboxyl groups of collagen in ordinary chrome tanning is due to John Arthur Wilson.

Further, in view of the danger of over simplification, it should also be noted that non-cationic chromium complexes are able to react with collagen and other substrates devoid of carboxyl ions[9]. Hence, evidently other protein groups are able to fix non-ionic and anionic chromium complexes and even the possibility of the participation of protein groups other than the carboxyl in secondary reactions involving the fixed cationic chromium complexes should not entirely be discounted.

As to the possibility of other protein groups, involved in ordinary chrome tanning besides the carboxyl, the hydroxy group present in considerable amounts in collagen is of great interest as it enters into hydrogen bonding. However, there is no disagreement with Shuttleworth and Cunningham in regard to the improbability of this group partaking in the cationic chrome tannage. The possible function of the hydroxy group, hinted at in the conclusion of my paper, was restricted to consideration of secondary reactions and particularly to the fixation of non-ionic chromium complexes, as evident from a recent paper[10]. It is suggested therein that the hydroxy group may be involved in the binding of non-ionic complexes of chromium to non-ionic protein groups. A probable indication of such a reaction is presented in the paper cited.

In conclusion, it seems advisable to accentuate that the uncertainty and limited knowledge of the chemistry and behavior of collagen as well as that of

tanning agents should leave ample room for diverging views, if those are kept within the compass of scientific principles and based on reliable experimental data. However, some restrictions seem to be needed in such cases where no safe basis of the views is established. In the best interest of leather chemistry, the following reflections should be justified: In a recent paper [11], a structural formula of the chromium complex supposed to be formed by boiling a solution of basic chromium sulfate with sodium sulfite and sodium oxalate has been presented together with structural formulae of a great many similar complicated compounds. These formulae have in fact as much experimental foundation as that of the structural formula of quebracho tannin advanced by the same author [12], claimed to be an improvement of Freudenberg's structure, which modification is put forward without any accompanying experimental data. The same type of claim is made for the structural formula of the mimosa tannin [13] also. The crowning event is the promulgation of a theory of vegetable tannage [13], in which the collagen model of Pauling and Corey* is handled. It is symtomatic that at the time of the appearance of this paper, the originators of the helical concept of protein structure had in so many essential points revised their views on the structure of collagen as to make any attempt of applying the merely tentative suggestion of collagen structure to complicated tanning reactions futile.

*Editor's Note: At the 50th Annual Meeting of the A.L.C.A. Pauling presented a revision of his concept of the collagen molecule.

Summary

The claim of Shuttleworth and Cunningham that the shift of the I.E.P. of collagen towards higher pH values produced by its combination with cationic chromium salts cannot be taken to indicate whether acidic or basic protein groups are involved, is shown not to be valid under the experimental conditions used in a previous investigation. In the technique used, the residual charge of the chromium complexes fixed by collagen which would interfere with the determination of the I.E.P. by methods based on the electrical charge of the chromed protein, had been eliminated since all free ions were removed prior to the determinations.

The uni- and multifunctional binding of polyvalent complex chromium cations by collagen, demonstrated by the interaction of chromium salts with gelatin, using ion exchangers, is mentioned.

Garverinaringens Forskningsinstitut,
Stockholm O, Sweden.

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Received, March 12, 1953

Tannage Factors and Their Effects On Leather Characteristics

By W. B. ZACHARIAS, C. W. MANN, E. T. STEINER and F. C. HORKOWITZ

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Department of the Army

INTRODUCTION

As a large consumer of leather products, the Office of The Quartermaster General needs to have available, for reference, reliable information on the more important properties of various types of leather used in military items. Since emergency conditions may require a reduction in the amounts of tanning materials normally used, or the use of synthetic tannins, information is needed on the effects of such variations on the characteristics of leather.

Many experimental tannages have been investigated and reported in the technical literature but, unfortunately, the data are widely scattered and many of the results are not directly comparable because of uncontrolled variables in the process. The application of much of the published information is generally very limited because of the small number of hides included in each experiment, and the large variability among the hides in each lot.

In cooperation with the National Research Council Advisory Committee on Quartermaster Research and Development, a program was initiated in 1948 to study the important variables in the tanning of side upper leather.

The project was designed to produce a series of experimental lots of leather for analysis and testing in the laboratory, for storage tests and for field evaluation in Army service footwear.

This paper presents a detailed report on the results of the laboratory tests on the experimental leathers. Subsequent reports will be made on the results of storage tests, service shoe wearing trials and the comparative evaluation of various combinations of natural and substitute tanning materials.

The Advisory Committee played an important part in planning the experiments and the members of the side upper leather industry also proved to be very helpful in guiding the choice of tannage factor levels as well as providing the detailed procedure required in each of the tannages under investigation.

Since many of the tannage factors were expected to have relatively small effects upon the leather properties, preliminary sampling studies were conducted in order to determine the best hide location from which specimens should be cut [1, 2]. The results made possible an increase in the precision of the tests and thereby improved the chances of detecting the effects of different treatments.

The series continually receives additional new tannages as they are made available from industry and research laboratories. To date, there have been processed 158 lots involving about 2300 sides.

Plan of Experiment

The specific object of study was a series of specially prepared leathers known as the US Experimental Leathers or USXL Series. The tannage factors selected for investigation were as follows:

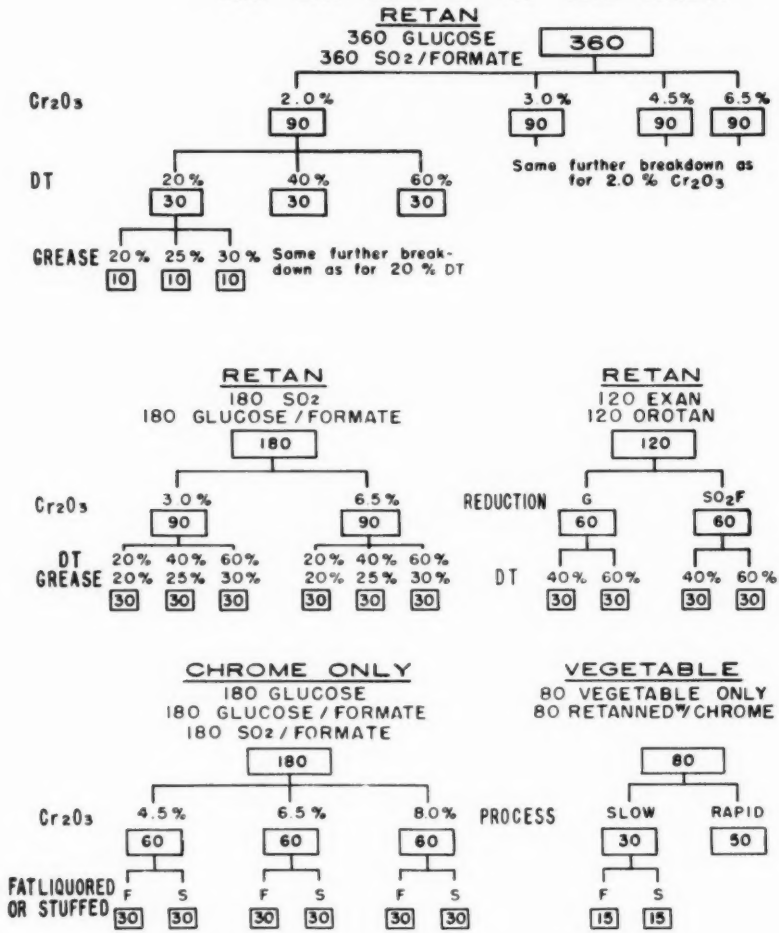
1. Types of Tannages.
   a. Chrome, vegetable or combination.
   b. Chrome, retannage with synthetic material.
2. Levels of Application.
   a. Tanning materials.
   b. Oils and greases.
3. Methods of Application.
   a. Rapid or slow vegetable tanning process.
   b. Glucose or sulfur dioxide reduction of chrome liquor.
   c. Chrome liquor with or without masking agent.
   d. Lubrication by stuffing or fatliquoring process.

Nearly half of the sides in this study were tanned by a combination chrome vegetable tannage of the type currently used for producing upper leather for Army service footwear. The series included systematic variations of chrome level, grease level and the degree of vegetable retannage. The chrome liquors for half of the retan leathers were reduced with glucose and those for the other half with sulfur dioxide. Each reducing agent was tried with and without a sodium formate masking agent, giving four reduction-masking treatments as in the following table:

Glucose Reduced		Sulfur Dioxide Reduced	
Masked	Unmasked	Masked	Unmasked
180 Sides	360 Sides	360 Sides	180 Sides

The scheme by which the 180 or 360 sides of each reduction group were further subdivided by tannage factor level is given in Figure 1 which also shows a similar breakdown for the 540 straight chrome tanned sides, for the 160 vegetable tanned sides, and for 240 chrome tanned sides which were synthetically retanned. In addition to these, about 300 other sides produced with synthetic or substitute materials have been submitted for evaluation and subsequently incorporated with the series.

FIG. 1. DISTRIBUTION BY TANNAGE FACTOR LEVEL OF THE FIRST 2020 SIDES OF THE USXL SERIES.



It will be noted that there were twice as many sides in the groups produced with unmasked glucose or masked sulfur dioxide as were included in the other groups. In the two smaller groups there was a balanced study of the effects of two factors, chromic oxide content in two levels and degree of tannage in three levels, giving six treatment combinations in all. Thirty sides were prepared in each of the six lots. Grease was applied in a measure appropriate to the degree of tannage. Thus all of the sides which were tanned to a degree of tannage of 20 were stuffed with 20 per cent grease, and so forth as in the following table:

Degree of Tannage	20	40	60
Corresponding Grease Level, Per cent (Dry Basis)	20	25	30

The two larger reduction groups (unmasked glucose and formate-masked sulfur dioxide) differ from the smaller groups in that:

1. Chromic oxide was studied in four levels instead of two.
2. A third factor, grease content, was studied in three levels independently of degree of tannage.

Each of the three degrees of tannage was compared with all four chrome levels and all three grease levels, giving 36 treatments in all. Thirty sides were prepared for each of the twelve combinations of chrome level and degree of tannage (4 x 3). The grease content was varied independently by dividing each lot of thirty sides into three groups of ten sides each and applying grease in three levels of 20, 25, and 30 per cent.

The straight chrome tanned sides were made up in eighteen lots of which nine were fatliquored and nine stuffed, each providing a balanced comparison of three reduction treatments and three levels of chrome.

The 160 sides of vegetable tanned leather were made up in six lots, half of which were retanned with unmasked glucose-reduced chrome. Of each group of 80 sides, 50 were produced by the new rapid method and 30 by the old, slow pit method. Fifteen of each of the two groups of 30 slow-process sides were fatliquored and fifteen were stuffed.

The treatments are summarized in the following table:

		Straight vegetable tanned	Retanned with Chrome
Rapid-processed	Stuffed	50 sides	50 sides
Slow-processed	Fatliquored	15 sides	15 sides
	Stuffed	15 sides	15 sides

The sides making up the USXL Series are not to be regarded as experimental curiosities. On the contrary, they are for the most part equivalent in quality

and acceptability to standard tannery output. They were produced under usual commercial conditions by tanners who had extensive experience in the production of side upper leather and large-scale methods were used whenever practicable.

It is true that the extreme factor levels studied lay well outside of the ranges that are commonly regarded as necessary to observe in order to produce acceptable commercial leather. The use of such low chrome content as 2.0 per cent, for example, or the use of such high grease content as 30 per cent with low degree-of-tannage led many to anticipate that a large percentage of the sides would be below par in acceptability. However, in view of the unusual levels of application of the tannage factors, it is noteworthy that a team of professional leather sorters, who were invited to pass judgement on the sides one by one, designated 57.4 per cent of the sides as acceptable for shoe manufacture. A large number of the remaining sides were unacceptable only because of discoloration or excessive grease.

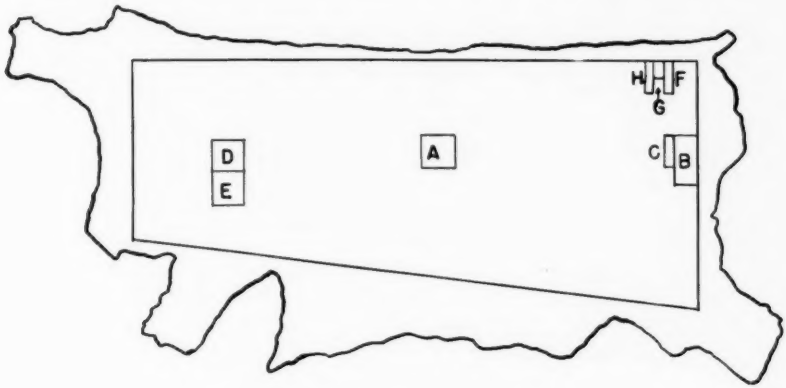
Test Methods

All of the physical tests commonly used for measuring the properties of upper leather were performed on each of the nearly 2300 sides. The selection of the test specimens from each side was made in accordance with the sampling plan for side upper leather described in a preliminary study [2]. The sampling locations are shown in Figure 1a.

The procedures followed in the physical testing were largely the official procedures described in Federal Specification KK-L-311. Exceptions are the Water Resistance, Water Vapor Permeability, Scuff Resistance, Grain Crack and the Burst Tests. Water resistance was measured on the Maeser apparatus [3]. Water vapor permeability was measured by the method developed by Kanagy and Vickers [4]. Scuff resistance was tested on the apparatus described by Mann [5]. The grain crack and one-inch-diameter burst loads were measured on a Tinius Olsen Testing Machine fitted with an adapter described in [6]. Finally the small diameter burst loads were measured on a Scott Tester adapted for the burst tests with a $\frac{1}{8}$ inch diameter plunger in conjunction with a $\frac{1}{2}$ inch orifice.

A composite sample of each lot of leather in the USXL Series was subjected to a chemical analysis for the usual constituents, including moisture, hide substance, ash, chromic oxide and grease. The grease levels treated in this report are the chloroform extracts, computed on a dry basis while chromic oxide is reported on a hide substance basis. The degree of tannage was calculated by the ALCA method for vegetable tanned leather except for the small amount of water soluble matter present which was included as combined tannin.

Figure 1a
SAMPLING LOCATIONS FOR UPPER LEATHERS



A BURST
B TENSILE STRENGTH & STRETCH
C STRESS STRAIN
D WATER VAPOR PERMEABILITY
E RESISTANCE TO WATER PENETRATION
F TONGUE TEAR
G STITCH TEAR
H DENSITY

Results and Discussion

How the Analyzed Values for the Tannage Factor Levels Compared with the Intended Values.

The tannage factor levels shown in Figure 1 are only nominal values as it is, of course, impossible to control the production of single lots of leather to exact requirements. The actual values obtained are shown in Table I which compares the analyzed values with the nominal values.

As expected, chrome and grease levels generally are in satisfactory agreement with the prescribed levels, whereas values for degree of tannage deviate considerably from the nominal values. The disagreement brought up the question of whether the results should be tablulated according to intended levels or according to actual values.

The results were analyzed first on the basis of nominal values. After the tannage factor effects were noted, a supplementary study of the relation between leather strength and tannage factor level was made using the actual analyzed values. The data for this supplementary study are given at the end of the section on degree of tannage.

TABLE I

Actual Analyzed Values for the Tannage Factor Levels.

Tannage	Reduction and Masking	NOMINAL VALUES OF THE TANNAGE FACTOR LEVELS											
		Degree of Tannage			Cr_2O_3 (% Hide Substance Basis)					$CHCl_3$ Extract (% Dry Basis)			
		20.0	40.0	60.0	2.00	3.00	4.50	6.50	8.00	Fatliquored	20.0	25.0	30.0
Retanned w/Veg	Glucose	34.4	45.3	61.2	2.42	3.16	5.04	6.06	——	——	22.7	25.4	29.7
	SO_2	36.7	53.9	56.4	——	3.24	——	6.70	——	——	23.4	25.0	26.6
	SO_2–Formate	31.4	44.8	54.2	2.44	3.93	5.17	6.37	——	——	24.1	26.9	29.8
	Glucose-Formate	32.8	40.8	52.7	——	3.97	——	6.80	——	——	24.5	26.1	31.1
Retanned w/Exan	Glucose	——	32.5	33.8	——	——	5.20	——	——	——	——	28.7	——
	SO_2–Formate	——	26.9	27.0	——	——	5.30	——	——	——	——	27.0	——
Retanned w/Orotan	Glucose	——	48.3	59.1	——	——	4.70	——	——	——	——	25.2	——
	SO_2–Formate	——	52.9	60.1	——	——	4.70	——	——	——	——	24.9	——
Straight Chrome	Glucose	——	——	——	——	——	4.05	6.40	8.85	7.9	——	26.6	——
	Glucose-Formate	——	——	——	——	——	4.60	6.40	7.55	8.8	——	25.9	——
	SO_2–Formate	——	——	——	——	——	4.60	6.70	7.45	8.8	——	27.2	——

As far as the effects of varying the levels of application of chrome, degree of vegetable retannage and grease are concerned, the conclusions reached in the supplementary study are virtually identical to those obtained by classifying test results according to nominal levels. Accordingly, it was decided to take advantage of the simplicity involved in using the nominal values when preparing the tables contained in this report. The only serious consequence of using intended values in place of actual values is in the case of the different methods of reducing the chrome liquors. This will be discussed in detail in the next section dealing with the chrome tannage.

The Effects of Variations in the Intensity of Chrome Tannage

It is well-known that the shrink temperature of leather is intimately connected with its chrome content. The results of this study show that in addition to its effect on the shrink temperature, the degree of chrome tannage also influences the strength and other characteristics of the leather. The results of the physical tests on chrome retan and straight chrome tanned leathers are presented in Tables II and III.

Retan Leather.

For all of the chrome retan leathers studied, the general trend in strength is downward as chrome concentration is increased. Retan leather containing 3 per cent chromic oxide is approximately 9% stronger in tongue tear strength and stitch tear strength than retan leather containing 6.5 per cent chromic oxide. These are average figures representing three different degrees of retannage and two methods of reducing the chrome, each used with and without sodium formate.

Figures 2(a), (b), (c) and (d) show a similar reduction in strength for the other strength tests.

In the burst, grain crack and tensile strength tests, glucose reduced, unmasked chrome retan leather seems to require special mention. The first column of Figure 2(b) indicates that this kind of leather does not follow the general trend of decreasing strength with increasing chrome content. However, more detailed results are presented in the last columns of Figure 2 which show the trend of the test results when chrome content is studied in four levels. For low concentration of chrome the usual downward pattern is observed, but when the chrome content is increased beyond 4.5% to 6.5%, there is a recovery of strength. In the above mentioned tests, there is enough of a recovery at 6.5% to bring the strength back to equal that of 3.0% chrome retan leather.

The curves in the bottom row of Figure 2(d) demonstrate that shrink temperature rises sharply with increasing chrome content for low concentrations of chrome but a break occurs in the curves near the 4.5% level above which there is little increase in shrink temperature with increasing chrome level.

TABLE II

Average Test Results for Retan Upper Leather

	Tongue Tear (lbs/in.)	Stitch Tear (lbs/in.)	Tensile Strength (10 lbs/in.2)	Grain Crack (lbs.)	1" Burst (lbs.)	1/8" Burst (lbs.)	Elongation (%)	Water Resistance (# flexes)	Water Vapor Perm'y (g/2500 cm²min)	Scuff Resistance (lbs.)	Shrink Temperature (C°)
GLUCOSE REDUCED											
2.0% chrome	311	862	378	522	999	117.0	67.7	173	.068	34.5	91.0
3.0% chrome	300	886	369	462	926	115.5	65.3	181	.066	26.8	95.3
4.5% chrome	286	836	353	410	912	109.2	60.4	183	.065	34.4	103.7
6.5% chrome	288	816	359	485	963	113.2	56.9	164	.076	31.3	104.6
20% DT	327	948	388	528	996	113.7	67.0	225	.053	29.7	99.0
40% DT	301	832	364	454	941	114.1	62.4	193	.067	32.5	98.8
60% DT	262	770	342	420	907	113.5	58.4	101	.086	33.3	98.9
20% grease	299	847	375	493	976	117.9	61.8	100	.093	29.9	98.3
25% grease	304	869	368	488	942	114.7	61.2	163	.068	37.6	99.4
30% grease	285	835	349	420	920	108.7	64.3	265	.046	28.4	99.0
Total	296	850	364	466	953	113.8	62.5	175	.069	31.9	89.0
FORMATE-MASKED SO_2											
2.0% chrome	319	901	382	522	1036	120.8	62.5	145	.081	30.0	92.6
3.0% chrome	282	904	377	474	1004	113.6	62.8	183	.071	31.4	100.2
4.5% chrome	269	907	349	420	986	120.0	57.2	156	.070	36.8	109.8
6.5% chrome	281	871	354	391	931	107.3	62.3	260	.069	29.9	111.8
20% DT	322	978	388	481	975	111.7	66.5	238	.047	28.0	101.0
40% DT	287	878	371	472	1018	118.9	60.3	184	.082	32.7	105.0
60% DT	263	843	344	403	964	114.2	58.4	251	.087	33.8	104.8
20% grease	283	901	374	453	986	117.9	61.5	105	.102	35.0	102.6
25% grease	290	891	366	448	982	115.5	58.6	213	.067	31.1	104.5
30% grease	290	892	356	447	991	112.0	64.0	251	.053	29.3	104.5
Total	288	895	366	449	987	115.1	61.3	190	.073	31.8	103.8

TABLE II—Continued

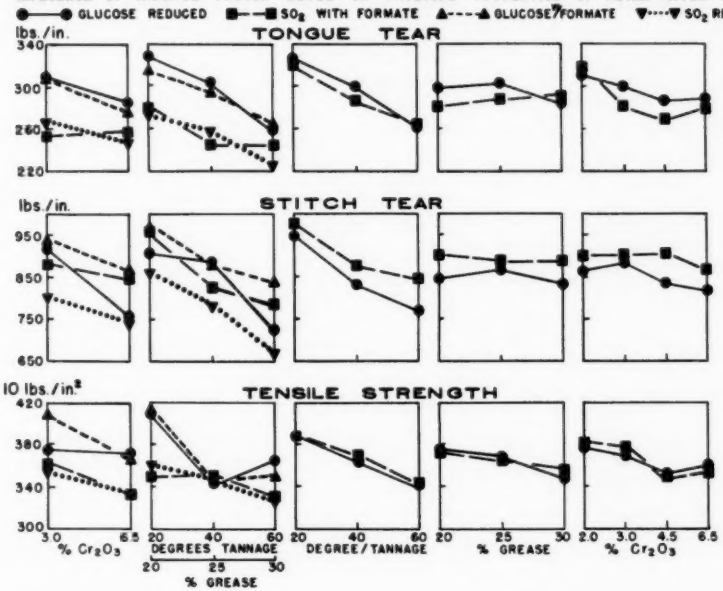
GLUCOSE REDUCED											
3.0% chrome	310	918	376	483	959	116.8	64.7	143	.074	25.6	95.0
6.5% chrome	286	759	373	533	1012	116.5	53.1	140	.076	27.2	104.2
20% DT–20% grease	329	907	410	563	1035	119.8	60.9	96	.092	25.5	99.2
40% DT–25% grease	305	887	345	452	930	117.0	61.3	188	.063	28.5	100.9
60% DT–30% grease	259	727	365	473	954	113.5	55.1	145	.070	25.2	98.7
Total	298	841	374	504	981	116.7	59.1	142	.075	26.4	99.5
SO_2 REDUCED											
3.0% chrome	268	801	356	481	927	111.3	55.9	110	.073	35.6	96.6
6.5% chrome	238	741	334	406	873	103.0	52.9	136	.068	26.8	109.8
20% DT–20% grease	276	863	361	475	944	110.5	58.1	88	.089	36.5	102.1
40% DT–25% grease	259	781	347	444	924	108.0	53.5	101	.072	29.8	104.3
60% DT–30% grease	224	671	327	409	828	103.0	51.7	154	.050	27.6	103.4
Total	253	771	345	443	900	107.2	54.4	121	.070	31.1	103.3
FORMATE-MASKED SO_2											
3.0% chrome	254	879	359	447	966	109.1	62.3	162	.074	30.7	100.3
6.5% chrome	257	839	332	349	882	103.9	60.7	244	.061	29.3	112.1
20% DT–20% grease	278	960	350	453	917	107.0	66.6	158	.065	29.3	103.3
40% DT–25% grease	244	824	350	380	922	106.3	58.7	243	.071	31.0	108.6
60% DT–30% grease	244	786	330	344	924	105.6	58.9	209	.066	29.5	107.8
Total	255	856	344	394	921	106.3	61.4	205	.067	29.9	106.6
FORMATE-MASKED GLUCOSE											
3.0% chrome	307	933	409	593	1044	124.3	57.2	111	.051	28.3	100.7
6.5% chrome	274	853	365	523	942	115.0	54.6	230	.046	28.1	113.6
20% DT–20% grease	315	966	412	630	1012	119.5	56.9	100	.057	27.8	105.6
40% DT–25% grease	294	878	397	611	1064	125.5	55.3	105	.062	28.7	107.8
60% DT–30% grease	263	834	349	435	904	114.0	55.4	305	.026	28.1	102.4
Total	291	892	387	558	993	119.7	55.9	173	.048	28.2	105.9

TABLE III

Average Test Results for Straight Chrome Tanned Upper Leather

	Tongue Tear (lbs/in.)	Stitch Tear (lbs/in.)	Tensile Strength (10 lbs/in.^{2})	Grain Crack (lbs.)	1" Burst (lbs.)	1/8" Burst (lbs.)	Elongation (%)	Water Resistance (# flexes)	Water Vapor Perm'y (g/2500 cm^{2}min)	Scuff Resist-ance (lbs.)	Shrink Temp-erature (C°)
GLUCOSE REDUCED											
Fatliquored	326	988	354	473	873	123.7	63.4	212	.297	30.5	96.4
Stuffed	435	942	387	378	1075	123.7	69.4	383	.011	30.0	105.7
4.5% chrome	426	1036	402	433	1043	122.4	63.6	238	.141	33.1	95.8
6.5% chrome	364	962	357	454	891	121.5	65.4	386	.175	30.7	100.0
8.0% chrome	354	898	351	385	1004	127.1	70.1	279	.161	26.7	107.4
Total	381	965	370	427	972	123.7	66.4	310	.159	30.2	101.1
FORMATE-MASKED GLUCOSE											
Fatliquored	358	1068	388	527	1029	132.3	67.1	220	.304	23.3	99.2
Stuffed	439	1042	412	385	1130	123.7	71.5	194	.021	26.0	108.7
4.5% chrome	421	1109	414	485	1115	128.5	67.7	180	.168	28.9	99.6
6.5% chrome	388	1056	411	428	1060	127.0	71.9	209	.159	22.3	105.1
8.0% chrome	385	1001	375	455	1064	128.5	68.2	232	.161	22.8	107.0
Total	398	1055	400	456	1080	128.0	69.3	206	.160	24.6	103.9
FORMATE-MASKED SO_2											
Fatliquored	363	1047	383	529	1008	126.0	70.8	214	.226	23.9	97.9
Stuffed	465	1020	404	480	1091	119.7	69.5	249	.022	27.5	106.8
4.5% chrome	429	1048	417	511	1033	125.5	71.3	296	.114	21.9	98.7
6.5% chrome	411	1043	398	509	1075	124.7	70.4	205	.128	27.2	103.8
8.0% chrome	402	1010	366	494	1040	119.0	68.7	198	.141	28.2	104.8
Total	414	1034	394	504	1049	123.0	70.1	234	.127	25.7	102.4

FIG. 2 (a)
INFLUENCE OF TANNAGE FACTOR LEVEL ON PHYSICAL PROPERTIES OF RETAN UPPER LEATHER

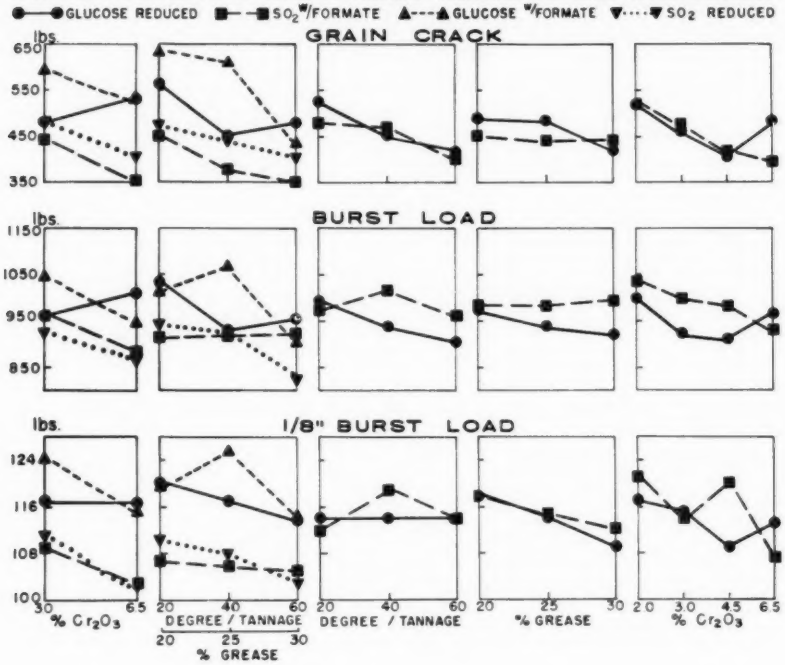


In the retan leather series, the reduction groups as a whole seem to differ in strength. The glucose reduction with formate gives the highest strength and the unmasked SO_2 the lowest. However, such apparent differences among reduction groups may be partially discounted since they result largely from the variation from one reduction group to another in degree of tannage. Table I shows that the actual and intended degree of tannage levels varied over a large range in this series. It happened that the glucose-formate lots received the lowest average degree of tannage, which, as shown below, results in the highest strength.

An analysis designed to evaluate differences among reduction groups after eliminating the influence of degree of tannage showed that residual differences were definitely present for some tests (e.g., tongue tear) but virtually absent for the majority including stitch tear and tensile strength.

The low water vapor permeability for glucose-formate retan leather is due partly to its relatively high grease content (see Table I). The low shrink temperatures associated with unmasked glucose reduction may be explained as a result of the low actual chrome levels.

FIG. 2 (b)
INFLUENCE OF TANNAGE FACTOR LEVEL ON PHYSICAL PROPERTIES OF RETAN UPPER LEATHER.

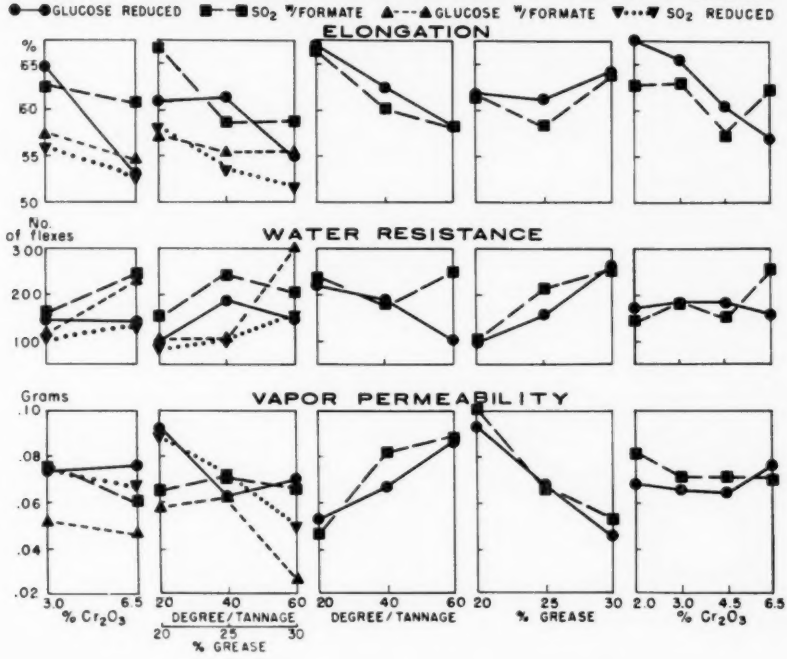


Straight Chrome Tanned Leather

The results of physical tests presented in Table III and Figure 3 show that low strength is associated with high concentrations of chromic oxide in the straight chrome tanned leather as in the case of retan leather. A study of average strength, as measured by tongue tear, stitch tear and tensile strength tests, shows that chrome leather containing 4.5% chromic oxide is approximately 10 per cent stronger than similar leather containing 8% chromic oxide. This same trend may be observed in each chrome reduction group. The results demonstrate that an increase in chrome level has approximately the same effect on the strength of straight chrome leather as on retan leather.

The general level of strength for unmasked glucose reduced chrome leather is 7.3% lower than for the two groups of lots masked with formate. Unmasked glucose reduction gives the best scuff resistance however. Figures 3(a) and (b) illustrate the trends in certain properties of chrome leather with increasing chrome level for three separate reduction-masking groups.

FIG. 2 (c)
INFLUENCE OF TANNAGE FACTOR LEVEL ON PHYSICAL PROPERTIES OF RETAN UPPER LEATHER.



The Effects of Variations in the Degree of Retannage

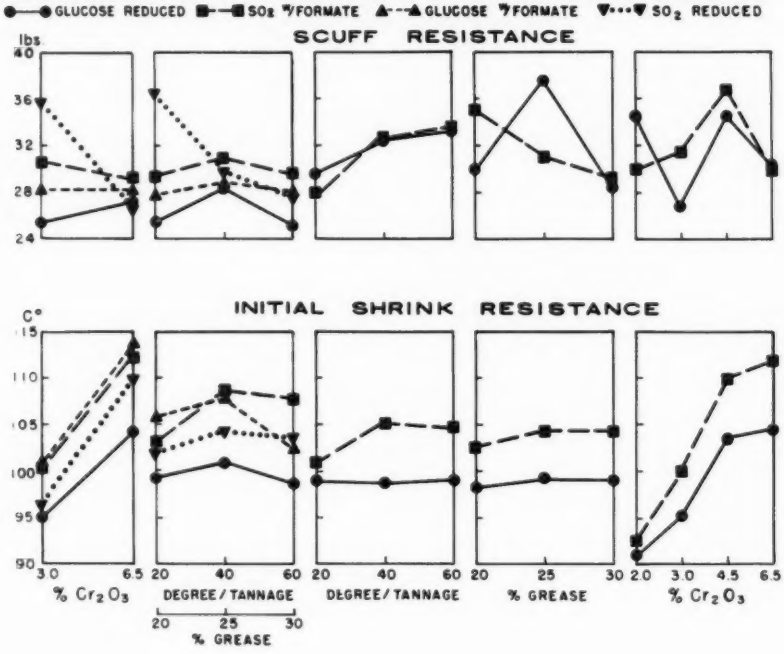
Retan Leather.

The results of the physical tests on chrome retan upper leather are presented in Table II. The effects of chrome level on shrink temperature and of grease level on water resistance and water vapor permeability were observed as expected in the retan leather. Somewhat surprising, however, was the pronounced effect which degree of tannage was observed to have on the strength of the leather. As the degree of retannage was increased, the strength of the leather decreased. Figures 1(a), (b), (c) and (d) show that the tear strengths were affected to the greatest extent and that tensile strength, load at grain crack and elongation at break also showed significant trends. The curves in the second column of Figures 2(a) to (d) trace the test values as the degree of tannage and grease level are increased together.

Whether it is appropriate to charge this downward trend to degree of tannage or to grease can be determined by considering the curves in Columns 3 and 4 which show results for the part of the USXL Series in which grease

FIG. 2 (d)

INFLUENCE OF TANNAGE FACTOR LEVEL ON PHYSICAL PROPERTIES OF RETAN UPPER LEATHER

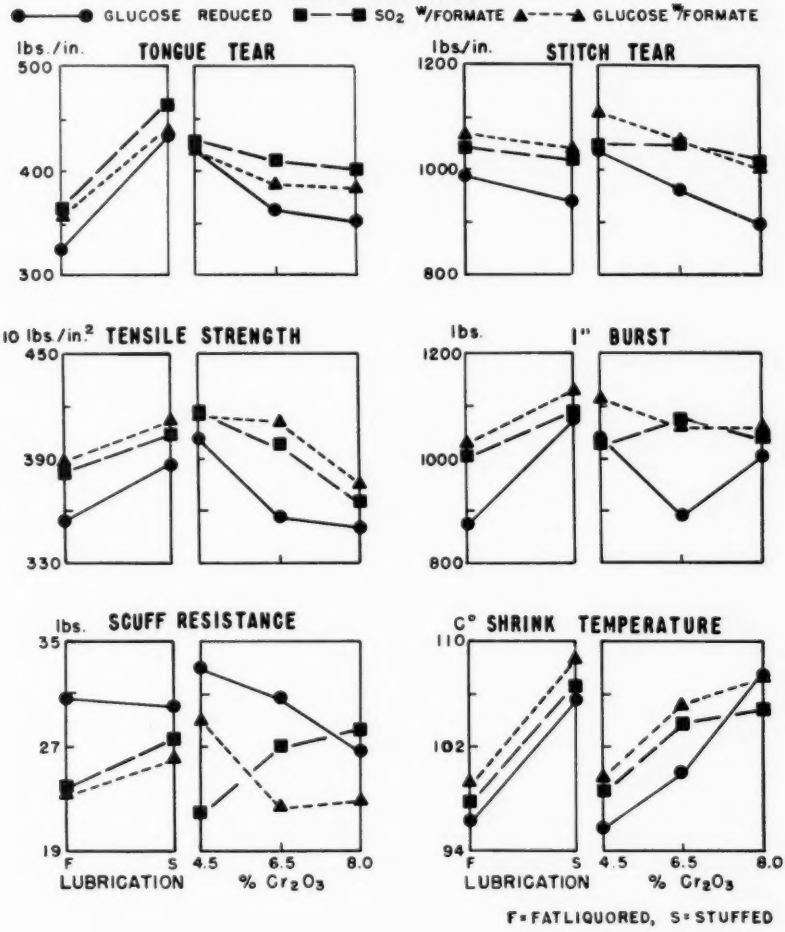


and degree of tannage were varied independently. It is of interest to see whether the downward slant of the curves of Column 2 is to be repeated the more faithfully in Column 3 or in Column 4. In the majority of the strength tests it is in the degree of tannage curves (Column 3) in which the strengths are seen to decrease with increasing level of application of the tannage factor. The grease curves (Column 4) are for the most part level which shows the very small or negative effect of a variation in grease content within the 20 to 30 per cent range. The only test in which high grease seems to be more influential than the high degree of tannage in lowering strength is the $\frac{1}{8}$" burst test.

Although grease had its anticipated effects on the water vapor permeability and water resistance, the degree of tannage also plays a role in these tests. The curves in Column 3 of Figure 2(c) show that if grease is held fixed and the degree of vegetable retannage is increased, the leather becomes more absorptive and therefore allows faster water penetration and greater permeability to water vapor.

FIG. 3

INFLUENCE OF TANNAGE FACTORS IN STRAIGHT CHROME UPPER LEATHER



The scuff resistance improves as the degree of tannage is increased if the grease level is held fixed (Column 3) Fig. 2(d). But, if grease is increased simultaneously with degree of tannage (Column 2), this tendency is nullified.

Chrome, Retanned with Synthetic Materials.

The results of the physical tests on the synthetically retanned leathers are presented in Table IV.

TABLE IV

Average Test Results for Chrome Tanned Upper Leather Retanned with Synthetic Materials

Test	Degree of Tannage	Exan Retanned		Orotan Retanned	
		G*	SF	G	SF
Tongue Tear	40%	306	320	333	307
(lbs/in.)	60%	310	319	314	351
Stitch Tear	40%	901	1026	961	860
(lbs/in.)	60%	870	1004	840	908
Tensile Strength	40%	403	404	430	408
(10 lbs/in.^{2})	60%	401	373	438	446
Grain Crack	40%	612	398	418	386
(lbs)	60%	540	394	569	478
1" Burst Load	40%	931	911	953	1060
(lbs)	60%	859	847	960	1136
1/8" Burst Load	40%	113	113	111	121
(lbs)	60%	111	112	123	142
Elongation at	40%	55.5	62.9	52.7	52.3
Break (%)	60%	58.3	63.3	48.9	50.8
Water Resistance	40%	300	241	521	205
(no. flexes)	60%	374	198	102	87
Water Vapor Perm'y	40%	.038	.036	.036	.036
(g/2500 cm^{2}min.)	60%	.042	.042	.060	.050
Scuff Resistance	40%	29.9	24.4	42.4	53.6
(lbs)	60%	27.0	24.8	42.1	55.0
Shrink Temperature	40%	105.8	106.1	103.2	104.4
(C°)	60%	102.5	109.1	101.7	103.4

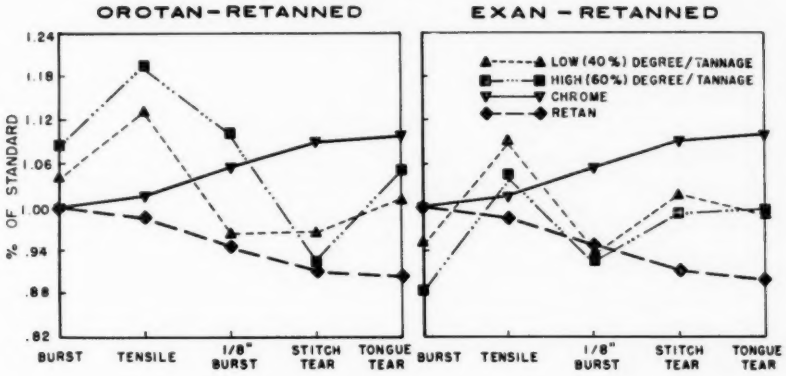
* G—Glucose Reduced Chrome
SF — SO_2 Reduced-Formate Masked Chrome

The effect of varying the degree of retannage with the synthetic material, Orotan, was relatively small and the pattern was not consistent from test to test nor from one reduction-masking group to another.

When the Orotan retannage was applied over glucose reduced chrome, the strength appeared to be independent of the degree of retannage except for stitch tear in which the low degree of tannage gave the stronger leather. For sulfur dioxide reduced chrome-Orotan leather it was the high degree of tannage lot which was stronger, being uniformly superior in all aspects of strength (see Table IV and Figure 4).

FIG 4

INFLUENCE OF DEGREE OF TANNAGE ON STRENGTH PROFILE OF SYNTHETICALLY RETANNED CHROME UPPER LEATHER



A high degree of retannage with Orotan produces an increase in water absorption as in the case of retannage with vegetable materials. A high degree of tannage in either case produces leather with relatively high water vapor permeability and low resistance to water penetration.

The USXL study included an evaluation of the synthetic material Exan as a substitute for vegetable tannin in Army retan upper leather. Production of this material has since been terminated.

The results of the physical tests on Exan retan leather, given in Table IV, indicate that when the retannage is with Exan, there are no material differences between lots retanned to a high degree and a low degree of retannage. This is shown in Figure 4 in which the two Exan curves follow each other rather closely. However, the conclusion is not valid as Table I shows that the actual figures for degree of tannage, obtained by difference, were identical for both the nominally high and low groups.

The Plumping Effect of Retannage.

The retanning of chrome leather with vegetable tannins is known to increase the plumpness of the leather. This has been suggested as an explanation for the relatively low strength associated with a high degree of tannage. As most strengths are measured in terms of load per unit thickness, any increase in thickness as a result of an increase in degree of retannage would result in a decrease in the strength thickness ratio unless accompanied by a corresponding increase in strength of individual fibers.

A study of the data shows that plumping plays only a small part in the effect of degree of tannage on the strength of retan leather. The supplementary study mentioned in the previous sections which was based upon actual

analyzed values of the tannage factor levels also served to evaluate the influence of plumping.

This supplementary study was a regression analysis of the lot averages for the 36 lots of glucose reduced retan leather. The results are given in Table V. For each of ten strength tests, there is listed in Table V a multiple correlation coefficient (R) and three coefficients of partial correlation.

TABLE V

The Influence of Chrome Level, Degree of Tannage and Grease Level on the Performance of Glucose-Reduced Chrome Retan Upper Leather on Various Strength Tests.

Strength Test	Multiple Correlation w/Test Scores (a Joint Index) R	Partial Correlations with Test Scores (Separate Indices) Degree of Chrome	Degree of Tannage	Grease
1″ Burst (lbs)	0.597	−0.232	−0.569	−0.339
1″ Burst (lbs/in.)	0.638	−0.251	−0.630	−0.242
Tongue Tear (lbs)	0.782	−0.592	−0.747	−0.265
Tongue Tear (lbs/in.)	0.783	−0.462	−0.771	−0.162
Tensile Strength (lbs)	0.614	−0.345	−0.528	−0.454
Tensile Strength (lbs/in.^{2})	0.653	−0.370	−0.605	−0.410
1/8″ Burst (lbs)	0.690	−0.458	−0.347	−0.653
1/8″ Burst (lbs/in.)	0.673	−0.392	−0.601	−0.492
Stitch Tear (lbs)	0.716	−0.546	−0.625	+0.137
Stitch Tear (lbs/in.)	0.702	−0.316	−0.665	+0.196

The multiple coefficients R show how effective the tannage factors, chrome level, degree of tannage and grease content, are in controlling the strength of the leather. R lies between 0 and 1, large values indicating tight control and small values indicating no control.

The coefficients of partial correlation show the separate effects of chrome, degree of tannage and grease on leather strength. These coefficients lie between −1 and +1, values near 0 indicating that the level at which that factor is applied is unimportant in determining the value of the physical property in question.

It will be observed that the tests in which the R's were largest are the tear tests. Thus, the levels of application of the tanning materials control the tear strength more effectively than they control burst and tensile strengths for glucose reduced retan leather.

The partial coefficients −0.592 and −0.232 found in the chrome column of Table V show that chrome has more to do with that characteristic measured by tongue tear load than with that measured by burst load.

The assertion was made earlier that, for purposes of evaluating the influence of tannage factor levels, it was unimportant to distinguish between nominal factor levels and actual levels. Justification for this assertion is now

provided by the exact correspondence of the above observations to the conclusions reached earlier from a consideration of the results classified according to nominal factor levels. The degree of tannage is shown in Table V to be the most important of the three tannage factors considered in determining the strength of the leather. The only exception is ⅛" plunger burst load in which grease is the dominating factor. The greater importance of grease in this test had been evident in Figure 2(b).

The ten strength tests of Table V result from giving a separate treatment to load data and to load per unit thickness data for each of five tests. The evidence that only a small part of the weakening which goes along with an increase in the degree of tannage is due to the increased plumping of the leather consists in the fact that the partial coefficients for degree of tannage are almost as strongly negative for the load tests as for those tests where strength was measured in terms of load per unit thickness.

The Effects of Variations in Vegetable Tannage

The results of the USXL experimentation on several types of vegetable tannage for upper leather are presented in Table VI. With the help of Table VI and Figure 5, evaluations can be made of the alternatives offered in each of the following comparisons:

a. Rapid process versus slow process in the tanning of vegetable leather.
   1. Straight vegetable leather.
   2. Vegetable leather retanned with chrome.

b. Fatliquoring versus stuffing for slow-process vegetable leather.
   1. Straight vegetable leather.
   2. Vegetable leather retanned with chrome.

c. Straight vegetable leather versus vegetable leather retanned with chrome.
   1. Rapid-process stuffed leather.
   2. Slow-process fatliquored leather.

It may be observed that rapid-process vegetable tanning produces weaker leather than does the regular process. Rapid-process leather elongates less before breaking. However, considering that the rapid-process leather was stuffed, the water vapor permeability is remarkably high, being almost as high as for fatliquored leather.

Retanning the vegetable leather with chrome increases the shrink temperature but lowers the high scuff resistance possessed by straight vegetable leather. As for its effect on strength, retanning the vegetable leather with chrome reduces further the strength of leather produced by the rapid method but strengthens the fatliquored slow-process leather.

TABLE VI

Average Test Results for Vegetable Tanned Upper Leather.

TEST	RAPID PROCESS Vegetable Tanned	RAPID PROCESS Retanned w/Chrome	SLOW PROCESS Vegetable Tanned		SLOW PROCESS Retanned w/Chrome	
	Stuffed	Stuffed	Stuffed	Fatliquored	Stuffed	Fatliquored
Tongue Tear (lbs/in.)	236	175	323	317	324	342
Stitch Tear (lbs/in.)	752	710	817	839	774	916
Tensile Strength (10 lbs/in.^{2})	379	323	411	475	386	477
Grain Crack (lbs)	460	526	572	483	300	408
1″ Burst Load (lbs)	849	670	1024	1086	1084	1410
1/8″ Burst Load (lbs)	112	97	120	133	121	156
Elongation at Break (%)	38.2	36.4	45.3	40.8	46.3	43.3
Water Resistance (# flexes)	82	85	38	64	78	107
Water Vapor Perm'y (g/2500 cm^{2}min.)	.226	.248	.044	.270	—	.280
Scuff Resistance (lbs)	69.2	54.1	51.3	77.9	30.3	27.6
Shrink Temperature (C°)	75.8	93.3	76.9	75.5	96.0	95.3

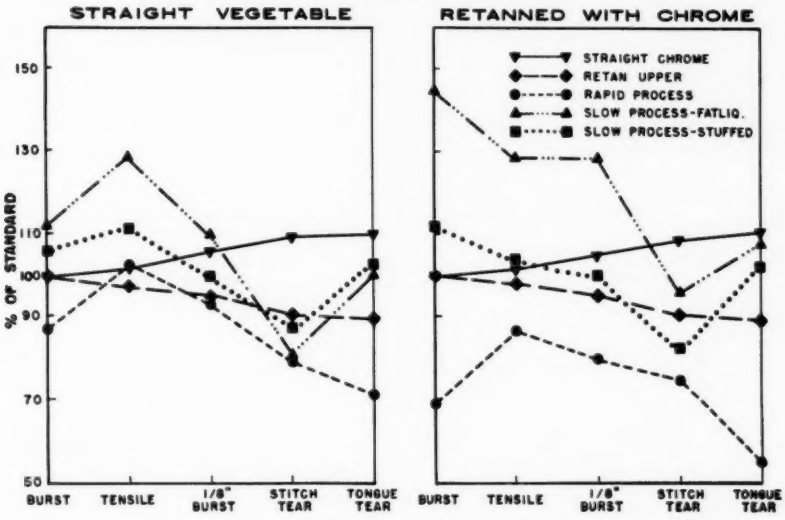
Fatliquored vegetable leather is somewhat stronger than that treated with a stuffing mixture. Particularly remarkable is the high burst strength of fatliquored vegetable leather when retanned with chrome, whether measured on the one inch or on the $\frac{1}{8}$ inch apparatus. Stuffed vegetable leather shows greater elongation and slightly higher shrink temperature than vegetable leather which is fatliquored.

Observations on the Characteristics of the Different Tannages

Besides providing the desired information on the extent to which tannage factor levels influence the physical properties of leather, the data collected in this study serve conveniently to compare the different basic tannages with each other. It is of interest to know which tannage produces the best tear strength, which the best scuff resistance or which is best for any desired combination of properties. For this purpose, Table VII was prepared showing comparative data for different tannages including straight chrome tannage,

FIG. 5

STRENGTH PROFILES FOR VEGETABLE TANNED UPPER LEATHER



straight vegetable tannage, chrome-vegetable retannage and vegetable tannage with a retannage of chrome (reverse retan). It was convenient to treat fatliquored and stuffed leather separately; therefore, eight different types of leather are compared. Only that vegetable leather produced by the slow-process is represented in Table VII. In presenting retan data, Table VII gives separate tabulations for vegetable retannage and for retannage with Orotan and Exan synthetic materials.

Figure 6 gives a graphic comparison of these eight basic tannages for each of the nine physical tests. The average value is marked at the center of the rectangle representing each particular tannage. The rectangle itself indicates the dispersion of the test values by showing the range of the middle two-thirds of the values. Some of the note-worthy facts revealed by Figire 6 are:

1. Chrome leather is quite stretchy and possesses good tear strength.
2. Vegetable leather is distinguished by low shrink temperature, high scuff resistance and low water resistance even when stuffed.
3. Retanning the vegetable leather with chrome improves the burst strength and shrink temperature but lowers the grain crack and scuff resistance.
4. Fatliquored vegetable leather has good tensile strength and good burst strength. Fatliquored vegetable leather retanned with chrome has particularly remarkable burst strength.

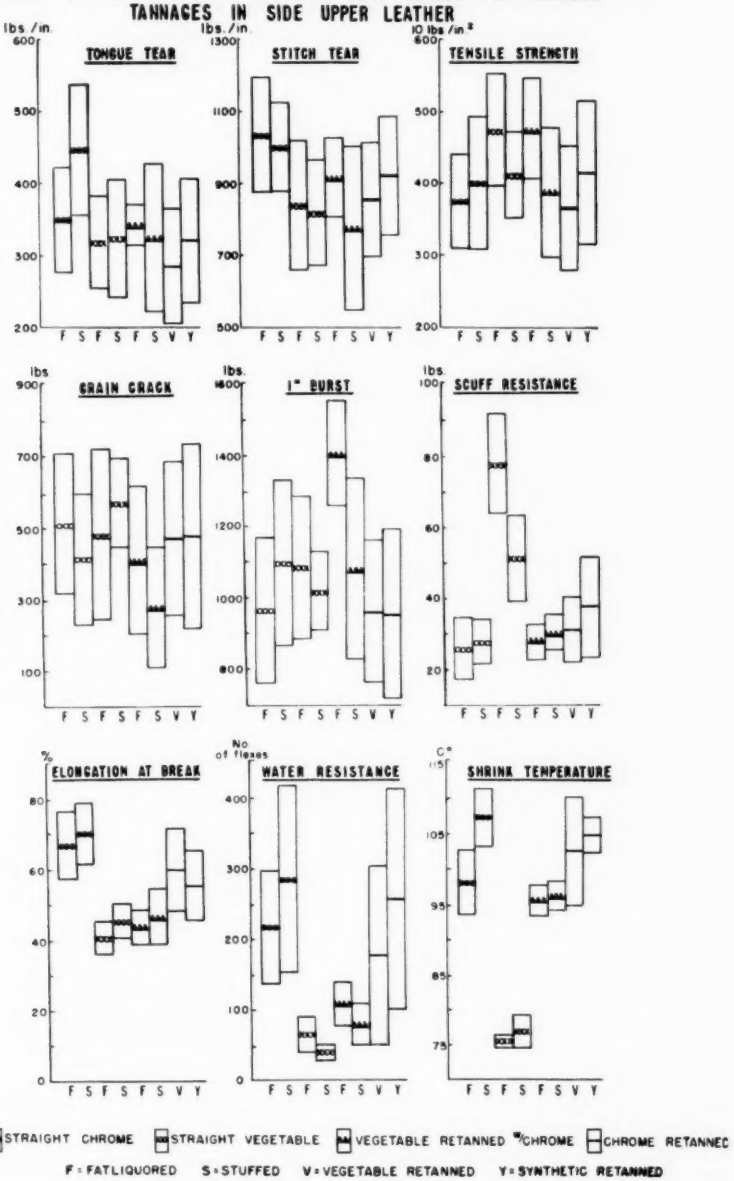
TABLE VII

The Relative Characteristics of Different Types of Tannage.

		STRAIGHT CHROME			STR. VEGETABLE			VEG. RET. W/CHR				ARMY RETAN		
	LUBR.	NO.	AV.	S.D	NO.	Av.	S. D.	NO.	AV.	S. D.	RET.	NO.	AV.	S.D.
Tongue Tear	Fatl	267	349	72	15	317	64	15	342	28	Veg	1063	285	80
(lbs/in.)	Stuf	268	446	91	15	323	82	14	324	103	Syn	208	320	86
Stitch Tear	Fatl	269	1035	160	15	839	180	15	916	109	Veg	1037	858	159
(lbs/in.)	Stuf	268	1001	125	15	817	147	14	774	227	Syn	209	930	167
Tensile Strength	Fatl	530	375	65	30	475	78	30	477	70	Veg	2123	365	87
(10 lbs/in.^{2})	Stuf	536	401	92	30	411	60	28	386	90	Syn	416	414	99
Grain Crack	Fatl	168	508	202	13	483	238	13	408	208	Veg	894	468	215
(lbs)	Stuf	166	413	184	13	572	125	13	300	192	Syn	144	474	261
1" Burst Load	Fatl	168	967	203	13	1086	203	13	1410	147	Veg	892	964	199
(lbs)	Stuf	166	1098	233	13	1024	112	13	1084	253	Syn	144	957	237
1/8" Burst Load	Fatl	251	127	16	13	133	——	13	156	——	Veg	1028	114	12
(lbs)	Stuf	223	122	15	13	120	——	12	121	——	Syn	211	118	——
Elongation at	Fatl	532	67.1	9.6	30	40.8	4.6	30	43.3	5.1	Veg	2122	59.7	11.7
Break (%)	Stuf	535	70.1	8.8	30	45.3	4.8	28	46.3	8.0	Syn	415	55.3	10.0
Water Resistance	Fatl	104	215	80	15	64	24	14	107	32	Veg	777	176	127
(# flexes)	Stuf	138	284	133	15	38	11	14	78	29	Syn	114	256	157
Water Vapor Per-	Fatl	45	.276	.046	5	.270	.012	5	.280	.025	Veg	398	.069	.032
meability (grams)	Stuf	43	.018	.015	5	.044	.005	—	——	——	Syn	40	.042	.022
Scuff Resistance	Fatl	259	25.9	8.8	14	77.9	13.9	14	27.6	5.2	Veg	1050	31.1	9.3
(lbs)	Stuf	254	27.8	6.6	15	51.3	11.7	14	30.3	5.1	Syn	206	37.3	14.2
Shrink Temper-	Fatl	264	97.9	4.6	14	75.5	1.2	15	95.3	2.2	Veg	1031	102.3	7.7
ature (C°)	Stuf	269	107.1	4.1	15	76.9	2.4	15	96.0	2.0	Syn	209	104.5	2.5

FIG. 6

EXTENT OF MIDDLE 2/3 OF PHYSICAL TEST VALUES FOR VARIOUS TANNAGES IN SIDE UPPER LEATHER



5. Fatliquored leather, whether chrome tanned or vegetable tanned, generally has higher stitch tear and water vapor permeability properties but low shrink temperature and slightly lower stretch than similar stuffed leather.
6. The tear strengths and tensile strength of retan leather are improved when the vegetable retannage is replaced by a retannage with either Orotan or Exan. A similar improvement in the average values for scuff resistance applies only to Orotan.

The Range of Variation in the Physical Properties of Leather

The Importance of Being Aware of Variability

Average test values for the many tannages investigated in the USXL study have been listed in Tables II, III, IV, and V. Many useful applications of the data require knowledge of more than just the average values, however.

For example, if a tanner should test 10 sides produced by an experimental modification of the usual tanning procedure and find the average tensile strength 15% higher than the level experienced with the usual process, is he justified in concluding that he has found a way to produce stronger leather? The answer to this may be yes or no depending on the extent to which tensile strength is inclined to vary even when an attempt is made to keep all controlling factors fixed. If there is a great deal of variability from side to side within a lot, all of whose sides received the same nominal tannage, then an apparent 15% improvement observed for ten sides may well have happened by pure chance when no basic improvement in the long run performance has been made. On the other hand, in tests like shrink temperature where there is relatively little variability once the tannage (specifically the chrome level) has been specified, the chances are very small that a sample of ten sides will show a 15% superiority in average shrink temperature unless some fundamental improvement in shrink temperature has really been made.

It is also important to know the range of variation when applying quality control methods to leather production. One must know how far apart to set the control limits and this requires a knowledge of how much the test values are inclined to vary even when conditions are at their best.

The Range of the Data Indicated by Two Standard Deviations

The usual way to indicate the range over which test data are spread is in terms of the standard deviation which is a sort of average deviation from the center of gravity of the data. The standard deviation is a large number if the data are widely scattered.

The complete tables which are found at the end of the article (Tables IX to XII) include two different standard deviations for each tannage group listed there. These are designated S and s.

The significance of these two standard deviations will be illustrated using stitch tear data from Table IXa. A line marked "total" appears at the end of each reduction-masking group. The value 135 in the s column for the "total" line under glucose reduction is the average value of the within lots standard deviations for the 36 lots of retan leather in which the chrome had been reduced with glucose. The number 135 indicates how much variability occurs among the sides in a typical lot of glucose reduced retan leather. Thus, two-thirds of the sides in a typical lot of glucose reduced retan leather will have stitch tear values concentrated in a range of length 2 x 135 = 270 lbs/in. centered about the lot average.

The within lots standard deviation, s, indicates variability which is more or less inevitable regardless of how well the tannage factors are controlled. This minimum variability is due mostly to natural differences among the animals furnishing the hides.

Proceeding to the S column, it will be noted that the value 159 lbs in. in the "total" row for glucose reduction is somewhat larger than the 135 found for s. This is because S is the standard deviation of all the sides of the 36 glucose lots lumped together into a single lot of 350 sides and all deviations are here measured from the grand average 850 lbs in. rather than each from its own lot average. S is much larger than s here because many different chrome levels and degrees of tannage are represented in the large lot and the individual lots making up the large lot differ considerably in average stitch tear strength due to these differences in tannage factor level. If the effects of tannage factor levels on stitch tear strength had been small, the lot averages would have been about the same regardless of variations in the tannage factors, then S and s would have been about the same size.

Separate S values also appear for the three degrees of tannage. The 144 lbs/in. for 20 degree of tannage is the standard deviation (S) for the lot obtained by pooling the sides from all the glucose reduced retan lots which received that degree of tannage. It will be observed that the S values 144, 135 and 145 for the separate DT groups, 20, 40 and 60 respectively, are smaller than the S value 159 which appears in the "total" line. This shows that controlling the degree of tannage gives increased control over the stitch tear values. The range 2 x 159 = 318 lbs/in. containing the middle two-thirds of the stitch tear values can be reduced to 2 x 145 = 290 lbs in. by specifying a 60 degree of tannage.

It will also be noted that the gap between S and s which was rather large for the "total" row is now much smaller. This narrowing of the gap as the degree of tannage is fixed gives further evidence of the importance of degree of tannage in controlling the stitch tear strength of retan leather. In each of the three degree of tannage groups, only chrome and grease are allowed to vary, the DT being held fixed at either 20, 40 or 60. The small gap between S and s for each of these groups means that further control of chrome level

and grease content will not add very much to the control of stitch tear to what stability has already been achieved by controlling DT.

Another test in which the gaps between S and s are of significant interest is the shrink temperature test (Table II(d)). Here it is in the homogeneous chrome groups rather than the DT groups where the gap between S and s is small. Since DT has little effect on the shrink temperature of retan leather, the gaps for the DT groups are as large as the gap in the "total" line.

Coefficients of Variation for the Physical Properties of Upper Leather

For some purposes, it is important to distinguish between s's which are large or small merely as a reflection of the average values ($\bar{x}$) and s's which are unusually large or small more or less independently of $\bar{x}$. The coefficient of variation ($s \div \bar{x}$) is widely used instead of s itself as a measure of reproducibility when it is desired to eliminate the influence of shifts in the magnitude of the average.

It was observed that values of the coefficient of variation computed are influenced only slightly by variation in the tannage factor level. However, the value for chrome leather as a whole may be appreciably different from the value for retan leather.

TABLE VIII

Values of the Coefficient of Variation $100\ s \div \bar{x}$ for some Physical Properties of Side Upper Leather

Physical Test	Type of Tannage			
	Chrome-vegetable retan, stuffed	Chrome Tanned, fat-liquored	Chrome tanned stuffed	Straight vegetable tanned
TONGUE TEAR (lbs/in.)	25.7	19.0	19.8	20.4
STITCH TEAR (lbs/in.)	15.7	14.8	10.8	18.9
TENSILE STRENGTH ($lbs./in.^2$)	22.1	16.2	22.2	16.4
GRAIN CRACK (lbs)	42.0	38.7	42.8	41.9
1" BURST LOAD (lbs)	20.0	19.7	20.9	17.0
ELONGATION AT BREAK (%)	17.1	12.1	12.3	12.7
VAPOR PERMEABILITY ($g/2500\ cm^2$-min)	24.8	7.7	52.2	9.5
SHRINK TEMPERATURE (C°)	2.4	2.4	1.4	2.6

The tables and formulae which give the number of sides required to be included in an experiment for the detection of a specified percentage difference between two lots of leather in some important property are often found given in terms of the coefficient of variation. For applications such as this, Table VIII is published showing coefficients of variation for eight physical properties of four common tannages for side upper leather.

Summary

The physical characteristics have been measured and compared on 2300 sides of upper leather produced in 158 lots, including straight chrome, straight vegetable and combination tannages.

Each of the more important tannage factors has been varied in graded levels to provide information on its effect on the properties of the leather. The results are presented in tables and graphs showing the trends in each of the physical properties with chrome level, retan level and grease level as well as the effects of other variables in the tanning process such as masking agents, method of reducing chrome liquors, fatliquoring versus stuffing and substitution of syntans in retan leather.

The results show the influence of tannage factor levels in different types of leather and furnish comparisons of the properties of chrome, vegetable and retan leathers.

Data are furnished on the range of variation, standard deviation and coefficients of variation for many types of side upper leather.

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The cooperation of the Endicott-Johnson Shoe Company, the International Shoe Company and the General Shoe Company in appraising the leathers for their commercial worthiness is acknowledged.

TABLE IX a

Properties of Retan Upper Leather

	TONGUE TEAR (lbs/in)				STITCH TEAR (lbs/in)				TENSILE STRENGTH (10 lbs/in²)			
	No. of sides (n)	Average (x̄)	Total s.d. (S)	w/lot s.d. (s)	No. of sides (n)	Average (x̄)	Total s.d. (S)	w/lot s.d. (s)	No. of sides (n)	Average (x̄)	Total s.d. (S)	w/lot s.d. (s)
GLUCOSE REDUCED												
2.0% chrome	87	311	86	78	86	862	128	108	174	378	94	82
3.0% chrome	86	300	76	70	86	886	140	121	172	369	73	70
4.5% chrome	98	286	76	70	89	836	191	160	194	353	84	78
6.5% chrome	89	288	80	79	89	816	162	142	178	359	79	75
20% DT	115	327	86	84	115	948	144	140	230	388	84	74
40% DT	121	301	78	76	121	832	136	121	242	364	83	79
60% DT	124	262	61	62	114	770	145	142	246	342	77	76
20% Grease	129	299	79	71	120	847	146	109	258	375	80	70
25% grease	112	304	82	75	111	869	151	120	224	368	91	84
30% grease	119	285	79	77	119	835	177	160	236	349	77	76
Total	360	296	80	74	350	850	159	135	718	364	83	76
FORMATE–MASKED SO_2												
2.0% chrome	87	319	81	76	87	901	128	118	173	382	91	82
3.0% chrome	83	282	84	73	84	904	152	125	168	377	85	76
4.5% chrome	77	269	62	62	68	907	123	119	156	349	72	67
6.5% chrome	104	281	79	73	94	871	158	141	205	354	77	73
20% DT	97	322	89	84	97	978	152	152	194	388	93	82
40% DT	126	287	76	68	116	878	129	117	250	371	80	76
60% DT	128	263	65	63	120	843	116	113	260	344	71	67
20% grease	119	283	77	66	108	901	140	122	236	374	87	75
25% grease	119	290	81	73	121	891	137	119	241	366	81	76
30% grease	113	290	80	75	104	892	152	140	227	356	79	73
Total	351	288	79	71	333	895	143	127	704	366	83	75

TABLE IX a (Cont'd)

	(n)	(£)	(S)	(s)	(n)	(£)	(S)	(s)	(n)	(£)	(S)	(s)
GLUCOSE REDUCED												
3.0% chrome	31	310	77	70	31	918	113	93	62	376	75	70
6.5% chrome	29	286	81	81	29	759	201	185	58	373	86	82
20% DT—20% grease	21	329	70	70	21	907	151	140	42	410	72	73
40% DT—25% grease	19	305	83	83	19	887	133	109	38	345	89	90
60% DT—30% grease	20	259	71	73	20	727	196	176	40	365	65	63
Total	60	298	79	75	60	841	179	145	120	374	80	76
SO_2 REDUCED												
3.0% chrome	85	268	67	65	85	801	153	136	170	356	83	83
6.5% chrome	88	238	65	60	88	741	150	123	176	334	67	63
20% DT—20% grease	56	276	72	71	56	863	170	172	112	361	80	80
40% DT—25% grease	59	259	57	54	59	781	111	98	118	347	71	70
60% DT—30% grease	58	224	65	63	58	671	112	109	116	327	74	72
Total	173	253	68	63	173	771	154	129	346	345	76	74
FORMATE-MASKED SO_2												
3.0% chrome	28	254	79	70	28	879	165	117	56	359	97	88
6.5% chrome	32	257	70	72	32	839	147	148	63	332	77	71
20% DT—20% grease	20	278	82	77	20	960	184	174	40	350	101	76
40% DT—25% grease	22	244	71	70	22	824	102	104	44	350	89	88
60% DT—30% grease	18	244	64	63	18	786	120	119	35	330	70	70
Total	60	255	81	71	60	856	156	135	119	344	88	79
FORMATE-MASKED GLUCOSE												
3.0% chrome	89	307	89	88	89	933	155	139	174	409	109	108
6.5% chrome	90	274	82	80	92	853	153	145	181	365	95	88
20% DT—20% grease	60	315	100	98	60	966	144	129	118	412	106	106
40% DT—25% grease	58	294	71	72	60	878	167	168	120	397	105	100
60% DT—30% grease	61	263	79	75	61	834	137	125	117	349	92	88
Total	179	291	87	83	181	892	159	142	355	387	104	99

TABLE IX—b

Properties of Retan Upper Leather

	GRAIN CRACK (lbs)				1" BURST LOAD (lbs.)				1/8" BURST LOAD (lbs.)	
	No. of sides (n)	Average ($\bar{x}$)	Total s. d. (S)	w/lot s. d. (s)	No. of sides (n)	Average ($\bar{x}$)	Total s. d. (S)	w/lot s. d. (s)	No. of sides (n)	Average ($\bar{x}$)
GLUCOSE REDUCED										
2.0% chrome	77	522	250	228	77	999	237	212	78	117.0
3.0% chrome	84	462	194	181	84	926	201	184	83	115.5
4.5% chrome	96	410	217	205	96	912	192	182	96	109.2
6.5% chrome	81	485	213	207	81	963	164	164	79	113.2
20% DT	113	528	254	223	113	996	210	182	111	113.7
40% DT	104	454	203	196	104	941	192	180	102	114.1
60% DT	121	420	191	194	121	907	193	190	123	113.5
20% grease	127	493	206	185	127	976	183	165	127	117.9
25% grease	94	488	258	246	94	942	221	212	91	114.7
30% grease	117	420	200	188	117	920	201	185	118	108.7
Total	338	466	222	205	338	953	201	186	336	113.8
FORMATE-MASKED SO_2										
2.0% chrome	85	522	231	228	85	1036	216	196	85	120.8
3.0% chrome	80	474	233	226	80	1004	205	198	81	113.6
4.5% chrome	76	420	157	152	76	986	178	177	77	120.0
6.5% chrome	100	391	158	158	100	931	192	189	102	107.3
20% DT	94	481	215	203	94	975	214	201	95	111.7
40% DT	122	472	206	195	122	1018	190	165	123	118.9
60% DT	125	403	200	184	125	964	199	205	127	114.2
20% grease	117	453	219	207	117	986	236	218	118	117.9
25% grease	113	448	198	189	113	982	172	173	115	115.5
30% grease	111	447	192	181	111	991	190	169	112	112.0
Total	341	449	203	193	341	987	201	190	345	115.1

TABLE IX—b cont'd

	(n)	(£)	(S)	(s)	(n)	(£)	(S)	(s)	(n)	(£)
GLUCOSE REDUCED										
3.0% chrome	31	483	210	212	31	959	205	204	28	116.8
6.5% chrome	22	533	148	131	22	1012	135	139	20	116.5
20% DT—20% grease	21	563	189	190	21	1035	178	183	19	119.8
40% DT—25% grease	12	452	245	247	12	930	226	236	9	117.0
60% DT—30% grease	20	473	126	127	20	954	140	137	20	113.5
Total	53	504	187	184	53	981	180	181	48	116.7
SO_2 REDUCED										
3.0% chrome	53	481	212	208	54	927	244	241	85	111.3
6.5% chrome	54	406	167	162	54	873	164	162	87	103.0
20% DT—20% grease	36	475	197	200	36	944	183	183	55	110.5
40% DT—25% grease	36	444	214	189	36	924	220	220	58	108.0
60% DT—30% grease	35	409	166	168	35	828	207	210	59	103.0
Total	107	443	194	186	107	900	207	205	172	107.2
FORMATE-MASKED SO_2										
3.0% chrome	27	447	269	244	27	966	234	231	27	109.1
6.5% chrome	31	349	157	158	31	882	184	174	31	103.9
20% DT—20% grease	20	453	271	229	20	917	272	239	20	107.0
40% DT—25% grease	20	380	187	190	20	922	170	156	20	106.3
60% DT—30% grease	18	344	184	184	18	924	185	186	18	105.6
Total	58	394	220	203	58	921	211	202	58	106.3
FORMATE-MASKED GLUCOSE										
3.0% chrome	54	593	244	237	54	1044	194	193	86	124.3
6.5% chrome	54	523	218	194	54	942	192	173	89	115.0
20% DT—20% grease	36	630	213	213	36	1012	181	175	58	119.5
40% DT—25% grease	36	611	211	214	36	1064	178	179	58	125.5
60% DT—30% grease	36	435	228	223	36	904	208	195	59	114.0
Total	108	558	233	217	108	993	199	183	175	119.7

TABLE IX—c

Properties of Retan Upper Leather

	WATER RESISTANCE (# FLEXES)				WATER VAPOR PERM'Y (g/2500cm²-min)				ELONGATION AT BREAK (%)			
	No. of sides (n)	Average (x̄)	Total s. d. (S)	w/lot s. d. (s)	No. of sides (n)	Average (x̄)	Total s. d. (S)	w/lot s. d. (s)	No. of sides (n)	Average (x̄)	Total s. d. (S)	w/lot s. d. (s)
GLUCOSE REDUCED												
2.0% chrome	70	173	134	102	39	.068	.030	.017	174	67.7	10.6	10.3
3.0% chrome	80	181	127	61	45	.066	.026	.014	172	65.3	10.9	9.1
4.5% chrome	80	183	157	100	45	.065	.034	.021	194	60.4	11.5	10.2
6.5% chrome	86	164	112	74	45	.076	.033	.015	178	56.9	10.7	8.9
20% DT	110	225	128	97	59	.053	.028	.013	230	67.0	11.8	10.5
40% DT	107	193	130	69	55	.067	.027	.018	242	62.4	10.9	9.1
60% DT	99	101	51	42	60	.086	.029	.020	246	58.4	10.9	9.3
20% grease	118	100	57	40	60	.093	.023	.019	258	61.8	11.5	9.5
25% grease	87	163	98	79	54	.068	.027	.016	224	61.2	10.5	9.2
30% grase	111	265	158	115	60	.046	.017	.016	236	64.3	12.8	10.2
Total	316	175	133	85	174	.069	.031	.017	718	62.5	11.7	9.6
FORMATE-MASKED SO_2												
2.0% chrome	84	145	102	57	45	.081	.036	.018	173	62.5	10.2	9.5
3.0% chrome	82	183	89	65	44	.071	.029	.016	168	62.8	9.4	8.4
4.5% chrome	64	156	75	66	30	.070	.025	.012	158	57.2	10.1	9.6
6.5% chrome	93	260	165	114	45	.069	.041	.019	205	62.3	12.8	10.1
20% DT	92	238	147	102	49	.047	.025	.016	194	66.5	10.4	9.3
40% DT	115	184	110	67	60	.082	.025	.016	250	60.3	10.1	8.7
60% DT	102	251	135	107	55	.087	.037	.018	260	58.4	11.1	10.3
20% grease	105	105	47	46	50	.102	.034	.019	236	61.5	10.7	9.2
25% grease	116	213	126	82	59	.067	.026	.017	241	58.6	11.0	9.6
30% grease	102	251	135	107	55	.053	.023	.014	227	64.0	10.8	9.3
Total	323	190	126	81	164	.073	.034	.017	704	61.3	11.0	9.5

TABLE IXc (Cont'd)

	(n)	($\bar{x}$)	(S)	(s)	(n)	($\bar{x}$)	(S)	(s)	(n)	($\bar{x}$)	(S)	(s)
GLUCOSE REDUCED												
3.0% chrome	29	143	81	63	15	.074	.023	.014	62	64.7	8.6	8.2
6.5% chrome	29	140	49	45	15	.076	.011	.009	58	59.1	8.5	8.2
20% DT—20% grease	20	96	26	23	10	.092	.011	.010	42	60.9	12.7	10.7
40% DT—25% grease	18	188	71	68	10	.063	.013	.011	38	61.3	8.1	6.7
60% DT—30% grease	20	145	61	63	10	.070	.014	.015	40	55.1	8.3	6.2
Total	58	142	66	55	30	.075	.018	.012	120	59.1	10.3	8.2
SO_2 REDUCED												
3.0% chrome	41	110	47	32	15	.073	.014	.012	170	55.9	10.3	9.8
6.5% chrome	28	136	68	56	15	.068	.029	.015	175	52.9	10.4	10.2
20% DT—20% grease	14	88	45	45	10	.089	.017	.015	112	58.1	11.8	11.7
40% DT—25% grease	26	101	35	35	10	.072	.010	.010	118	53.5	11.8	10.8
60% DT—30% grease	29	154	62	60	10	.050	.019	.015	115	51.7	6.9	6.9
Total	69	121	57	49	30	.070	.022	.014	345	54.4	10.4	10.0
FORMATE-MASKED SO_2												
3.0% chrome	28	162	83	65	15	.074	.017	.014	56	62.3	7.5	7.5
6.5% chrome	31	244	105	62	15	.061	.018	.015	63	60.7	13.9	11.4
20% DT—20% grease	19	158	50	49	10	.065	.023	.015	40	66.6	10.0	8.2
40% DT—25% grease	22	243	135	62	10	.071	.015	.013	44	58.7	11.0	9.9
60% DT—30% grease	18	209	82	77	10	.066	.018	.018	35	59.8	11.4	11.2
Total	59	205	103	63	30	.067	.018	.015	119	61.4	11.3	9.8
FORMATE-MASKED GLUCOSE												
3.0% chrome	33	111	36	33	15	.051	.023	.016	174	57.2	11.4	10.5
6.5% chrome	36	230	183	96	15	.046	.025	.015	181	54.6	11.2	10.8
20% DT—20% grease	22	100	21	21	10	.057	.021	.018	118	56.9	12.7	11.5
40% DT—25% grease	23	105	37	37	10	.062	.021	.018	120	55.3	10.7	10.0
60% DT—30% grease	24	305	184	116	10	.026	.011	.009	117	55.4	10.7	10.5
Total	69	173	147	75	30	.048	.024	.015	355	55.9	11.4	10.7

TABLE IX—d

Properties of Retan Upper Leather

	SCUFF RESISTANCE (lbs)				SHRINK TEMPERATURE (C°)			
	No. of side (n)	Average (x̄)	Total s.d. (S)	w/lot s.d. (s)	No. of sides (n)	Average (x̄)	Total s.d. (S)	w/lot s.d. (s)
GLUCOSE REDUCED								
2.0% chrome	86	34.5	13.6	7.5	86	91.0	2.4	2.3
3.0% chrome	86	26.8	6.0	5.2	85	95.3	2.7	2.4
4.5% chrome	103	34.4	8.4	6.5	98	103.7	2.9	2.5
6.5% chrome	89	31.3	10.1	6.5	89	104.6	2.2	1.9
20% DT	115	29.7	8.0	5.6	115	99.0	6.2	2.6
40% DT	120	32.5	11.3	6.8	120	98.8	6.2	2.1
60% DT	129	33.3	10.9	6.9	123	98.9	6.4	2.2
20% grease	129	29.9	8.5	6.0	129	98.3	5.8	2.1
25% grease	116	37.6	11.4	7.4	110	99.4	6.5	2.6
30% grease	119	28.4	8.5	6.0	119	99.0	6.5	2.2
Total	364	31.9	10.3	6.5	358	89.9	6.2	2.3
FORMATE-MASKED SO_2								
2.0% chrome	85	30.0	7.2	5.7	86	92.6	2.4	1.9
3.0% chrome	80	31.4	8.3	6.2	84	100.2	3.0	2.3
4.5% chrome	78	36.8	8.4	6.8	79	109.8	2.5	1.7
6.5% chrome	101	29.9	7.5	6.1	102	111.8	2.4	1.8
20% DT	94	28.0	6.7	5.5	96	101.0	8.7	2.0
40% DT	123	32.7	7.7	5.8	125	105.0	8.1	1.9
60% DT	127	33.8	8.9	7.0	130	104.8	7.3	1.9
20% grease	118	35.0	8.6	7.2	119	102.6	8.0	1.9
25% grease	114	31.1	8.5	6.0	119	104.5	8.6	2.1
30% grease	112	29.3	6.5	5.2	113	104.5	7.8	1.8
Total	344	31.8	8.3	6.2	351	103.8	8.2	2.0

TABLE IX—d (cont'd.)

	(n)	($\bar{x}$)	(S)	(s)	(n)	($\bar{x}$)	(S)	(s)
GLUCOSE REDUCED								
3.0% chrome	31	25.6	5.9	5.7	30	95.0	2.0	1.9
6.5% chrome	29	27.2	6.9	5.1	29	104.2	2.7	2.4
20% DT—20% grease	21	25.5	4.6	4.5	21	99.2	4.3	2.1
40% DT—25% grease	19	28.5	7.0	5.2	18	100.9	6.1	2.8
60% DT—30% grease	20	25.2	7.1	6.4	20	98.7	4.2	1.4
Total	60	26.4	6.4	5.4	59	99.5	5.2	2.1
SO_2 REDUCED								
3.0% chrome	83	35.6	10.2	6.5	85	96.6	2.9	2.9
6.5% chrome	86	26.8	4.5	4.5	88	109.8	2.7	2.0
20% DT—20% grease	53	36.5	12.1	5.9	56	102.1	6.4	2.3
40% DT—25% grease	58	29.8	5.8	5.5	59	104.3	7.9	2.2
60% DT—30% grease	58	27.6	5.6	5.4	58	103.4	7.1	2.9
Total	169	31.1	9.0	5.6	173	103.3	7.2	2.5
FORMATE-MASKED SO_2								
3.0% chrome	26	30.7	5.8	5.4	28	100.3	3.0	1.6
6.5% chrome	31	29.3	6.9	6.2	32	112.1	2.4	1.6
20% DT—20% grease	20	29.3	7.0	7.0	20	103.3	6.7	1.4
40% DT—25% grease	19	31.0	6.8	6.1	22	108.6	6.3	1.9
60% DT—30% grease	18	29.5	5.4	3.9	18	107.8	5.3	1.4
Total	57	29.9	6.4	5.9	60	106.6	6.5	1.6
FORMATE-MASKED GLUCOSE								
3.0% chrome	85	28.3	6.0	6.0	89	100.7	3.1	2.9
6.5% chrome	88	28.1	10.4	9.7	60	113.6	3.7	2.9
20% DT—20% grease	59	27.8	11.3	11.4	60	105.6	6.6	3.3
40% DT—25% grease	57	28.7	8.0	6.2	60	107.8	8.5	3.0
60% DT—30% grease	57	28.1	5.2	5.1	29	102.4	1.6	1.6
Total	173	28.2	8.5	8.1	149	105.9	7.1	2.9

TABLE X—a

Properties of Chrome Tanned Upper Leather

	Tongue Tear (lbs/in)				Stitch Tear (lbs/in)				Tensile Strength (10 lbs/in²)			
	No. of sides (n)	Average ($\bar{x}$)	Total s. d. (S)	w/lot s. d. (s)	No. of sides (n)	Average ($\bar{x}$)	Total s. d. (S)	w/lot s. d. (s)	No. of sides (n)	Average ($\bar{x}$)	Total s. d. (S)	w/lot s. d. (s)
GLUCOSE REDUCED												
Fatliquored	87	326	66	55	89	988	151	142	178	354	60	56
Stuffed	90	435	88	83	89	942	129	118	179	387	93	91
4.5% chrome	59	426	88	75	59	1036	125	124	120	402	75	73
6.5% chrome	60	364	106	79	60	962	144	144	118	357	86	83
8.0% chrome	58	354	72	55	59	898	124	122	119	351	70	70
Total	177	381	95	71	178	965	142	130	357	370	80	76
FORMATE-MASKED GLUCOSE												
Fatliquored	90	358	67	67	90	1068	156	152	177	388	65	64
Stuffed	88	439	92	89	89	1042	123	111	179	412	93	91
4.5% chrome	58	421	89	74	59	1109	140	141	117	414	82	81
6.5% chrome	60	388	87	73	60	1056	124	125	120	411	79	77
8.0% chrome	60	385	90	87	60	1001	138	135	119	375	78	78
Total	178	398	90	78	179	1055	141	134	356	400	81	79
FORMATE-MASKED SO_2												
Fatliquored	90	363	78	78	90	1047	164	164	175	383	65	63
Stuffed	89	465	92	93	90	1020	100	93	178	404	89	85
4.5% chrome	60	429	104	90	60	1048	155	154	120	417	70	69
6.5% chrome	59	411	96	84	60	1043	126	122	116	398	79	78
8.0% chrome	60	402	98	82	60	1010	125	122	117	366	78	78
Total	179	414	99	86	180	1034	136	133	353	394	78	75

TABLE X—b

Properties of Chrome Tanned Upper Leather

	GRAIN CRACK (lbs)				1" BURST LOAD (lbs)				1/8" BURST LOAD (lbs)	
	No. sides (n)	Average (x̄)	Total s. d. (S)	w/lot s. d. (s	No. of sides (n)	Average (x̄)	Total s. d. (S)	w/lot s. d. (s)	No. of sides (n)	Average (x̄)
GLUCOSE REDUCED										
Fatliquored	60	473	245	237	60	873	214	210	83	123.7
Stuffed	58	378	162	162	58	1075	231	220	62	123.7
4.5% chrome	36	433	167	166	36	1043	203	150	48	122.4
6.5% chrome	46	454	261	241	46	891	263	249	48	121.5
8.0% chrome	36	385	182	184	36	1004	232	223	49	127.1
Total	118	427	213	204	118	972	244	215	145	123.7
FORMATE-MASKED GLUCOSE										
Fatliquored	54	527	174	177	54	1029	187	186	84	132.3
Stuffed	54	385	158	155	54	1130	262	266	84	123.7
4.5% chrome	36	485	191	188	36	1115	264	266	56	128.5
6.5% chrome	36	428	179	160	36	1060	209	206	56	127.0
8.0% chrome	36	455	170	149	36	1064	222	211	56	128.5
Total	108	456	180	167	108	1080	232	230	168	128.0
FORMATE-MASKED SO_2										
Fatliquored	54	529	170	172	54	1008	166	169	84	126.0
Stuffed	54	480	213	217	54	1091	204	204	77	119.7
4.5% chrome	36	511	219	219	36	1033	199	200	56	125.5
6.5% chrome	36	509	183	184	36	1075	198	188	49	124.7
8.0% chrome	36	494	180	183	36	1040	173	171	56	119.0
Total	108	504	193	196	108	1049	189	187	161	123.0

TABLE X—c

Properties of Chrome Tanned Upper Leather

	Elongation At Break (%)				Water Resistance (No. Flexes)				Water Vapor Permeability (g/2500 cm² – min)			
	No. of sides (n)	Average ($\bar{x}$)	Total s. d. (S)	w/lot s. d. (s)	No. of sides (n)	Average ($\bar{x}$)	Total s. d. (S)	w/lot s. d. (s)	No. o sides (n)	Average ($\bar{x}$)	Total s. d. (S)	w/lot s. d. (s)
GLUCOSE REDUCED												
Fatliquored	178	63.4	9.6	7.6	40	212	93	86	15	.297	.045	.031
Stuffed	179	69.4	8.7	8.8	54	383	129	108	14	.011	.010	.008
4.5% chrome	120	63.6	9.1	7.1	30	238	89	64	10	.141	.143	.028
6.5% chrome	118	65.4	9.8	8.5	39	386	156	122	10	.175	.179	.021
8.0% chrome	119	70.1	8.9	8.8	25	279	116	93	9	.161	.132	.017
Total	357	66.4	9.6	8.2	94	310	142	99	29	.159	.149	.023
FORMATE-MASKED GLUCOSE												
Fatliquored	178	67.1	8.9	7.8	34	220	85	49	15	.304	.024	.020
Stuffed	178	71.5	8.2	8.1	42	194	57	57	15	.021	.014	.010
4.5% chrome	117	67.7	10.2	8.3	29	180	54	47	10	.168	.161	.017
6.5% chrome	120	71.9	7.8	7.8	22	209	56	57	10	.159	.133	.019
8.0% chrome	119	68.2	7.8	7.7	25	232	92	57	10	.161	.155	.010
Total	356	69.3	8.8	7.9	76	206	72	53	30	.160	.145	.016
FORMATE-MASKED SO_2												
Fatliquored	176	70.8	9.0	9.1	30	214	53	40	15	.226	.016	.015
Stuffed	178	69.5	9.3	9.0	42	249	108	71	14	.022	.018	.008
4.5% chrome	120	71.3	8.6	8.6	25	296	97	71	10	.114	.109	.006
6.5% chrome	116	70.4	9.9	9.9	22	205	68	60	9	.128	.112	.014
8.0% chrome	118	68.7	8.9	8.7	25	198	68	47	10	.141	.103	.014
Total	354	70.1	9.2	8.2	72	234	90	60	29	.127	.105	.012

TABLE X—d

Properties of Chrome Tanned Upper Leather

	Scuff Resistance (lbs)				Shrink Temperature (C°)			
	No. of sides (n)	Average ($\bar{x}$)	Total s.d. (S)	w/lot s.d. (s)	No. of sides (n)	Average ($\bar{x}$)	Total s.d. (S)	w/lot s.d. (s)
GLUCOSE REDUCED								
Fatliquored	85	30.5	10.1	8.1	87	96.4	5.7	2.8
Stuffed	85	30.0	7.2	5.5	90	105.7	4.9	1.4
4.5% chrome	59	33.1	8.8	6.7	58	95.8	5.2	2.0
6.5% chrome	56	30.7	8.7	6.3	59	100.0	5.3	2.0
8.0% chrome	55	26.7	7.7	7.7	60	107.4	5.1	2.4
Total	170	30.2	8.8	6.9	177	101.1	7.1	2.2
FORMATE-MASKED GLUCOSE								
Fatliquored	89	23.3	6.4	5.0	90	99.2	3.9	2.4
Stuffed	82	26.0	5.5	5.2	89	108.7	3.5	1.4
4.5% chrome	55	28.9	5.4	5.5	59	99.6	4.9	1.7
6.5% chrome	57	22.3	5.7	5.4	60	105.1	5.0	1.8
8.0% chrome	59	22.8	4.8	4.2	60	107.0	5.5	2.4
Total	171	24.6	6.1	5.1	179	103.9	6.0	2.0
FORMATE-MASKED SO_2								
Fatliquored	85	23.9	7.8	7.8	87	97.9	3.5	2.0
Stuffed	87	27.5	6.3	4.6	90	106.8	3.1	1.8
4.5% chrome	59	21.9	4.4	4.4	59	98.7	5.0	1.5
6.5% chrome	55	27.2	8.4	7.8	59	103.8	5.0	1.9
8.0% chrome	58	28.2	6.9	6.4	59	104.8	4.7	2.2
Total	172	25.7	7.3	6.3	177	102.4	5.6	2.0

TABLE XI

Properties of Synthetically Retanned Chrome Upper Leather

	RETANNED WITH EXAN							RETANNED WITH OROTAN						
		Glucose Red'n			Masked SO_2 Red'n			Glucose Red'n			Masked SO_2 Red'n			
	Deg Tann. (%)	No. of sides (n)	Average (x̄)	Stnd. devn. (s)	No. of sides (n)	Average (x̄)	Stnd. devn. (s)	No. of sides (n)	Aver. age (x̄)	Stnd. devn. (s)	No. of sides (n)	Average (x̄)	Stnd. devn. (s)
Tongue Tear	40	28	306	80	25	320	82	26	333	82	26	307	91
(lbs/in.)	60	25	310	71	25	319	97	28	314	63	25	351	114
Stitch Tear	40	28	901	101	25	1026	174	26	961	142	26	860	156
(lbs/in.)	60	25	870	114	25	1004	246	28	840	164	26	908	120
Tensile Strength	40	58	403	92	50	404	109	52	430	82	52	408	100
(10 lbs/in^2)	60	50	401	81	46	373	88	56	438	102	52	446	114
Grain Crack	40	18	612	290	18	398	209	18	418	207	18	386	253
(lbs.)	60	18	540	263	18	394	162	18	569	303	18	478	301
1″ Burst	40	18	931	201	18	911	207	18	953	190	18	1060	213
Load (lbs)	60	18	859	178	18	847	128	18	960	237	18	1136	366
1/8″ Burst	40	28	113	—	25	113	—	26	111	—	26	121	—
Load (lbs)	60	27	111	—	25	112	—	28	123	—	26	142	—
Elongation At	40	58	55.5	8.0	50	62.9	10.8	52	52.7	8.8	52	52.3	9.5
Break (%)	60	50	58.3	7.8	45	63.3	3.3	56	48.9	6.2	52	50.8	8.2
Water Resistance	40	15	300	77	15	241	90	14	521	122	13	205	37
(no. flexes)	60	15	374	149	15	198	46	14	102	47	13	87	29
Water Vapor Permeability	40	5	.038	.009	5	.036	.005	5	.036	.015	5	.036	.009
(grams)	60	5	.042	.011	5	.042	.009	5	.060	.010	5	.050	.029
Scuff Resistance	40	28	29.9	6.2	25	24.4	5.7	26	42.4	5.9	25	53.6	9.2
(lbs)	60	25	27.0	4.7	25	24.8	4.7	28	42.1	9.5	24	55.0	15.5
Shrink Temperature	40	29	105.8	1.7	24	106.1	1.1	26	103.2	0.8	26	104.4	1.1
(C°)	60	25	102.5	1.1	25	109.1	0.8	28	101.7	1.5	26	103.4	1.4

TABLE XII

Properties of Vegetable-Tanned Upper Leather

		All Vegetable			Retanned w/Chrome		
		No. of sides (n)	Average ($\bar{x}$)	Stnd. Dev'n (s)	No. of sides (n)	Average ($\bar{x}$)	Stnd. Dev'n. (s)
TONGUE	Rapid	49	236	46	41	175	30
TEAR	Reg-Fatl.	15	317	64	15	342	28
(lbs/in.)	Reg-Stuffed	15	323	82	14	324	103
STITCH	Rapid	50	752	108	39	710	129
TEAR	Reg-Fatl.	15	839	180	15	916	109
(lbs/in)	Reg-Stuffed	15	817	147	14	774	227
TENSILE	Rapid	60	379	51	60	323	52
STRENGTH	Reg-Fatl.	30	475	78	30	477	70
(10 lbs/in.^{2})	Reg-Stuffed	30	411	60	28	386	90
GRAIN	Rapid	18	460	162	18	526	156
CRACK	Reg-Fatl.	13	483	238	13	408	208
(lbs)	Reg-Stuffed	13	572	125	13	300	192
1" BURST	Rapid	18	849	124	18	670	161
LOAD	Reg-Fatl.	13	1086	203	13	1410	147
(lbs)	Reg-Stuffed	13	1024	112	13	1084	253
ELONG'N	Rapid	60	38.2	5.1	60	36.4	4.3
AT BREAK	Reg-Fatl.	30	40.8	4.6	30	43.3	5.1
(%)	Reg-Stuffed	30	45.3	4.8	28	46.3	8.0
WATER	Rapid	10	82	9	10	85	17
RESISTANCE	Reg-Fatl.	15	64	24	14	107	32
(# Flexes)	Reg-Stuffed	15	38	11	14	78	29
WATER VAPOR	Rapid	5	.226	.088	5	.248	.033
PERMEABILITY	Reg-Fatl.	5	.270	.012	5	.280	.025
(g/2500 cm^2 min)	Reg-Stuffed	5	.044	.005	—	—	—
SCUFF	Rapid	50	69.2	13.3	39	54.1	12.0
RESISTANCE	Reg-Fatl.	14	77.9	13.9	14	27.6	5.2
(lbs)	Reg-Stuffed	15	51.3	11.7	14	30.3	5.1
SHRINK	Rapid	44	75.8	2.7	38	93.3	3.0
TEMPERATURE	Reg-Fatl.	14	75.5	1.2	15	95.3	2.2
(C°)	Reg-Stuffed	15	76.9	2.4	15	96.0	2.0
1/8" BURST	Rapid	50	112	—	39	97	—
LOAD	Reg-Fatl.	13	133	—	13	156	—
(lbs)	Reg-Stuffed	13	120	—	12	121	—

The laboratories of the National Bureau of Standards, the Tanners' Council and Lehigh University were instrumental in sampling and performing many of the chemical and physical tests on the USXL leathers.

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Discussion

President Koppenhoefer: I think you will all agree that this was a tremendous task. The mass of data which has been accumulated here are most impressive. If there is a discussion at this time, I am sure Mr. Zacharias will be most glad to answer questions.

Mr. William T. Roddy (Cincinnati, Ohio): I think Mr. Zacharias might mention that the leathers, while experimental, were definitely made in a tannery under the best conditions that were available and while all of the leathers did not particularly meet the original requirements, they at least, in any given series, come fairly close to it.

Would you care to mention a little more about the set-up of the leathers as made in the tannery?

Mr. Zacharias: Of course, a great deal of care went into this. A good many people were consulted, and I really have not given the credit that is due.

What you say is quite correct. The people who made the chrome retan lots were tanners who specialize in chrome retan leather work. The tanners who made the straight chrome lots were accustomed to making that type of leather. I am sure that these were all made under the very best conditions.

Mr. Roddy: That is not particularly the approach I had in mind. We had occasion at Cincinnati to make cross sections of most of these leathers and I would like to say, on the basis of cross sections, that they compare very favorably with commercial chrome and vegetable leathers, and chrome and vegetable retan leathers, that are normally placed on the market. That is the point I would like to emphasize.

Mr. Balfour: When you speak of varying your degree of tannage, do you differentiate between your degree of tannage due to chromium and degree of tannage due to your retan? And how do you raise them? Do you raise one or raise both?

Mr. Charles W. Mann: I might answer that question. This was a systematic test in which the chrome and retan were varied independently. We included one lot of low chrome leather retanned to a low degree of retannage, a second lot of low chrome leather retanned to a medium degree of retannage and a third lot retanned to a high degree of retannage. The variables chrome

and retan were separated in the analysis. In the results that you saw on the slides, the effect indicated for retannage was the effect of the retannage alone on chrome leather in which other factors were held constant. As Mr. Zacharias said, there was some confounding through the combining of variables in some cases. For example, the grease content was equalized in some lots by the following method. With 20 degree of retannage the grease level was 20 per cent. With 40 degree of retannage the grease level was 25 per cent. And with 60 degree of retannage the grease level was 30 per cent.

The analysis of these lots does not disclose whether the differences are due to grease content or degree of tannage. Those factors are confounded but we did separate them in some of the other parts of the test in which grease content and degree of tannage were independent.

DR. LOLLAR: Would it be a generally safe summary to state that as the load on the hide substance was increased the physical strength characteristics tended to decrease?

MR. ZACHARIAS: Yes, that is a safe general summary. Moreover, increasing the load on the Hide Substance lowered not only the strength figures expressed on a per inch thickness basis, but also lowered the pure undivided load figures—showing that this phenomenon is not to be charged to the plumpness of Retan leather with high degree of vegetable retannage. In straight chrome leather, increasing the chrome concentration lowered the strength also.

The Separation of Pigments and Fillers From Mineral Tanning Agents

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Over the last decades the analysis of chrome tanned leather has become increasingly complex. Innes and Sheppard [1] have pointed out that inaccuracies and difficulties are inherent in the official method of the Society of Leather Trades' Chemists for the determination of aluminum in chrome leather. In their work the so-called wet oxidation with perchloric acid compared favorably with the older fusion method which employed a borax mixture. Küntzel & Kuhtz [2] studied these two alternatives at about the same time. Both investigations suggested a more correct way of obtaining the aluminum content of chrome leather. Innes and Sheppard developed a colorimetric method for it while Küntzel and Kuhtz precipitated in one sample the mixed hydroxides of Al and Cr, estimated the chrome in a separate wet oxidized solution and obtained the aluminum oxide by difference.

The present method of the American Leather Chemists' Association covers the possible presence of iron which is not discussed at all by the above authors, but it is not fully aware of the pitfalls which in the light of these papers surround the determination of chrome and alum when they occur together in leather.

Preliminary Investigations

All three procedures have one defect in common which in connection with mineral leather analysis becomes more and more serious. Metallic tanning agents cannot be separated from pigments and fillers containing those same metals in the form of silicates or oxides. Both classes of materials are employed together today in many possible combinations. Colloidal Clay which is a hydrated aluminum silicate*, is frequently associated with aluminum. Iron is likely to be present in leather in the form of oxides or of compounds with tanning properties; yet no method discussed above allows a separation of both. French Chalk** can easily be taken for clay when associated with aluminum as is frequently the case in white leathers.

The limit of perfection which can be achieved with the aid of the dry fusion method has been reached by Somerville and Wendkos[3] analyzing heavily pigmented zirconium leathers. Only two of the nine ingredients of a composite mixture, simulating the ash which may conceivably be obtained from such a leather, go in solution by leaching out the fusion with water. The balance comprising the tanning agent itself as well as pigments like TiO_2, chalk and talcum, dissolve in acid whereas the components of one, clay, are found in both fractions.

Similar complications arise from an attempt to base the estimation of the possible ingredients of today's leather on the wet oxidation method. Here the four principal mineral tanning agents, chrome, iron, aluminum and zirconium, would, of course, be in the soluble fraction. Barium sulfate, on the other hand, would stay insoluble. As far as talcum and titanium dioxide are concerned experiments disclosed that they are partially attacked by the perchloric acid-sulfuric acid mixture regardless of the presence or absence of chrome.

It was felt, in view of these results, that the digestion of leather with weak mineral acids would be a more promising approach to the entire problem. Dilute mineral acids would dissolve the leather without attacking its pigments and fillers, at least not to the extent a wet oxidation would. Figures obtained in this way, i. e. by hydrolyzing clay-filled leathers with 2.0 *N* H_2SO_4, are shown in the Table I opposite the percentages for those insolubles which resisted the wet oxidation and which are largely silicon dioxide.

*Arbitrary formula: $Al_2O_3.2SiO_2.2H_2O$–composed of 39.5% Al_2O_3, 46.5% SiO_2 and 14% H_2O.

**A fine type of talc with the arbitrary formula $3MgO.4SiO_2.H_2O$–composed of 44% MgO, 49.5% SiO_2 and 6.5% H_2O (see Lange's Handbook of Chemistry, 7th Ed., p. 252)

TABLE I

Colloidal Clay in Chrome Leather

State of Leather	Insolubles in dil. H_2SO_4 computed as % clay in air dry leather.	Remaining after wet oxidation	
		Insolubles as % of air dry leather.	% SiO_2 in insolubles.
(a) Undyed, sample A	5.66	3.2	75
" B	8.32	4.7	79
(b) Colored, sample C	4.25	1.6	100
" D	9.85	5.0	84

On the other hand, there was still proof lacking that clay is absolutely inert towards mineral acid in the dilution employed above for digesting leather. However, if 2.0 *N* sulfuric acid, or for that matter, any other acid or combination of acids in the proper concentration, were to permit the analysis of tanning agents without interference from most pigments and fillers, this possibility was certainly worthy of being pursued further. Consequently, the first purpose of a study aimed at this goal was to ascertain whether or not dilute sulfuric acid is the proper agent for the determination of clay in leather.

Development of New Analytical Methods

When clay was boiled with various acids it was quickly found that sulfuric acid attacks it more than some organic acids and that formic acid does not dissolve clay at all. A few figures illustrating these findings are shown in Table II.

TABLE II

Recovery of Colloidal Clay after Boiling with Acids

Per cent of total clay (0.1g) dissolved by boiling with:	
2.0 *N* sulfuric acid (approx. 10% by vol.)	5.8%
saturated oxalic acid (approx. 10% by vol.)	4.7%
Mixture of equal volumes of 2.0 *N* trichloracetic acid and 2.0 *N* formic acid	2.3%
2.0 *N* formic acid (102 g/l)	none

Unfortunately, formic acid canot be used for the digestion of leather because of extreme difficulties in filtering the resulting hydrolysate. These were overcome by combining the action of formic acid with that of trichloracetic acid. Nearly 98 per cent of the clay was unattacked by this mixture and the filtrate presented no problem when wet oxidized and analyzed for mineral tanning agents.

The following Table III allows a full comparison of the digestive action of sulfuric acid and the above mentioned organic acid mixture upon leather.

TABLE III

Clay and Aluminum Oxide Content of Leather Dependent on Method of Digestion

Digestion Medium	% coll. clay	% chromic oxide occluded on clay	% alum. oxide (Al_2O_3)	coprecip. with Al_2O_3 % chromic oxide	coprecip. with Al_2O_3 % ferric oxide
a) 2.0 *N* sulfuric acid	6.52	0.02	4.96	0.07	0.77
b) 1.0 *N* formic/1.0 *N* CCl_3COOH mixture	8.80	0.04	3.11	0.13	0.62
difference	2.28		1.85 equal to 2.16% colloidal clay		
c) 2.0 *N* formic	9.00				
d) 1.0 *N* CCl_3COOH	8.77				

The aluminum hydroxide precipitate in the filtrate as well as the insolubles representing clay were both fused and analyzed for occluded Fe and Cr.

Table III shows that for practical purposes:

1. the amounts of chrome found in the clay precipitate are negligible.
2. the coprecipitation of small amounts of chrome with the alum is unavoidable. In the example of Table III they comprise 1.3 and 2.4 per cent respectively of the total chrome found.
3. Al_2O_3 cannot be computed correctly without taking into account the soluble iron present as a contaminant which coprecipitates with the aluminum hydroxide.
4. sulfuric acid dissolves much more clay (in the example of Table III over 25 per cent more) than could be anticipated from Table II, where the action of sulfuric acid upon clay in absence of leather is shown.
5. the organic acid mixture dissolves as much clay as either of its two components. At the same time it speeds up the filtration of insolubles which proceeds very slowly when either of the 2 components is used by itself.
6. there can be no doubt that the treatment with sulfuric acid leads to an exaggerated figure for Al_2O_3. In fact, when this increase is apportioned to clay where it belongs, it almost matches the deficit observed there as Table III clearly shows.

From the conclusions which are summarized above, the investigation proceeded into two directions; several pigments and fillers were subjected to the digestion with the newly found mixture, from now on referred to as FTA, and leathers tanned principally with iron or zirconium were treated likewise.

Only barium sulfate and titanium oxide were found to be totally resistant to the action of FTA. Bentonite and iron oxide go into solution sparingly, while talcum and Silene (calcium silicate of Pittsburgh Glass Co.) are fully hydrolyzed; in their case the insoluble portion is almost pure SiO_2. No work substantiating these findings on leather itself has been conducted so far, in view of the very limited scope of application and importance of Silene and talcum for chrome leather.

Examples of a colored leather pigmented with iron oxide and of iron-tanned leather are given in Table IV.

TABLE IV

Iron Oxide Pigment vs. Iron Tannage in Leather Analysis

	Remaining insoluble after digestion with FTA			Precip. by NH_4OH in wet oxidized soluble fraction		
	% Iron Oxide	% Chromic Oxide	% Other Oxides	% Iron Oxide	% Chrome Oxide	% Al_2O_3
a) Before Pigmentation	0.26	0.06	0.09	0.12	0.06	3.96
After Pigmentation	11.6	0.10	2.8[1]	0.12	0.10	3.38
b) Iron-Aluminum-Chrome Combination Tannage	0.15	0.05[3]	3.26[2]	6.25	0.20[3]	0.62

(1) evidently associated with the iron oxide

(2) this is really clay; hence, equivalent to 3.79 per cent colloidal clay in the hydrated stage

(3) there was also 0.77 per cent Cr_2O_3 in the filtrate from the hydroxide precipitate; hence, the total Cr_2O_3 amounted to 1.02 per cent of which 25 per cent was found in the two precipitates obtained by the procedure, an unuausly high percentage.

It is apparent that iron-tanned leather can be easily discerned from leather pigmented with iron. This is particularly important because both iron tannage and iron pigments can be found together occasionally. By the new method it also becomes possible to investigate the layerwise distribution of iron pigments in leather even when it is tanned or contaminated with iron salts.

Finally, zirconium tanned white suede leather was digested with FTA in the same way as the other tannages. The result was disappointing: very little went into solution. When only 2.0 *N* sulfuric acid was employed the figures for Zr were as high as those received by dry or wet oxidation of the leather. Sulfuric acid, however, would be of little use for pigmented leather because it also dissolves some clay. The dilemma was solved by utilizing the unique property of hydroxyacids whose complexes with many metals, including Zr, are water soluble over the whole pH range. A fairly strong hydroxyacetic (glycolic) acid solution served successfully for the separation of Zr and clay as Table V shows.

TABLE V

The Separation of Clay and Zirconium Oxide by Various Acids

Digestion Acid	% Insolubles after Digestion	% Zirconium Oxide in sol. fraction
2.0 *N* H_2SO_4	8.6	13.2
FTA	20.6	1.2
4.0 *N* glycolic	9.1	13.4
Ashing and Dry Fusion	——	13.1
Direct Wet Oxidation	——	13.6

It may be pointed out that the so-called insolubles in this table may comprise clay as well as titanium oxide. The filtrate of the glycolic acid digestion, on the other hand, is free of titanium. Glycolic acid therefore offers a very satisfactory separation of Zr and pigment although it is not as universally applicable as the formic-trichloracetic acid mixture ("FTA") used heretofore. This became evident when Ponolith, which is a frequent ingredient of white leathers, was analyzed for ZnS by digesting 0.05 g. of it with FTA. The results of this treatment are summarized in Table VI. The figures show that the acidity of glycolic acid is insufficient for decomposing all ZnS in the pigment.

TABLE VI

The Action of Glycolic Acid and FTA Upon Ponolith

	Unattacked portion of pigment in % of total pigment used	% $BaSO_4$ + inert material in Ponolith (a)	% ZnS by diff. (b)	% ZnS dissolved by acid (c)	% of total ZnS not attacked (d)
4.0 *N* Glycolic Acid	84	72	12	16.8	42
"FTA"	74	72	2	26.4	7

Note: $d=\frac{100b}{b+c}$ Specif. for Ponolith: appr. 28% ZnS, 71% $BaSO_4$

Experimental leather, containing various amounts of Ponolith as the only mineral ingredient besides chrome, was subjected to digestion with the aid of the acids under discussion. As in the case of the pigment itself, with the exception of sulfuric acid they were not potent enough for dissolving all the zinc present, although FTA was much better than glycolic acid. The figures received in this series of experiments are compiled in Table VII.

TABLE VII

Action of Various Acids Upon Ponolith Pigmented Chrome Leather

	% Insolubles ($BaSO_4$ fraction)	% ZnS (Soluble Fraction)	Sum	% of Total ZnS retained in $BaSO_4$ fraction
Leather A	a	b	a+b	c
2.0 *N* H_2SO_4	2.2	1.08	3.28	none
FTA	2.4	0.94	3.34	13
Leather B				
2.0 *N* H_2SO_4	7.3	3.36	10.66	none
FTA	8.3	2.40	10.70	28
4.0 *N* Glycolic	9.75	0.72	10.47	79

Note: c is computed as the per cent difference between the figures for b (%ZnS) obtained on each leather with 2.0 *N* H_2SO_4 and with other acids.

(for instance $\frac{1.08-0.94}{1.08} \times 100 = 13\%$)

Since glycolic acid was found indispensable for the analysis of Zr leathers, it was of interest to test this acid on titanium tanned leather as well. The leather sample which was available for this investigation, had been tanned with basic titanium sulfate and retanned with formaldehyde. It carried 7.3 per cent TiO_2 as the wet oxidation method disclosed. Boiling with 2.0 *N* H_2SO_4 gave much lower values because of the hydrolysis taking place at this concentration. Only when the strength of the sulfuric acid was increased to 6.0 *N* was it possible to bring most of the titanium in solution, namely 93 per cent. 4.0 *N* glycolic acid solution was also very inefficient. Here, by raising the strength to 8.0 *N*, some more titanium was brought into solution, namely 76 per cent. Titanium dioxide pigment is not attacked by any of these solutions. Thus it is quite feasible to separate soluble and insoluble titanium in leathers by hot acid digestion, although here glycolic acid is less efficient than with the other mineral tanning agents.

After exploring these specific applications of glycolic acid solutions, it seemed necessary to investigate their usefulness for ordinary chrome leather as well as for leather pigmented with iron oxide. However, complications arose which make it advisable to abide by the use of FTA for all but zirconium tanned leathers. First of all, difficulties in filtering were encountered with some leathers containing organic fillers. Besides, the glycolic acid partly dissolves iron oxide and therefore is unsuitable for the separation of soluble and insoluble iron in leather. A breakdown in the analysis of brown chrome leather serves to illustrate this point (Table VIII). Although the amount of iron pigment is small, not exceeding 0.2 per cent about two-thirds of it are dissolved by the hydroxy acid. Moreover, it appears from the figures for Al_2O_3 and clay that glycolic acid may hydrolyze a little clay.

TABLE VIII

The Action of Glycolic Acid and FTA Upon Chrome Leather

Acid Employed	% Fe_2O_3 in insol. fraction	% Fe_2O_3 in sol.	% Cr_2O_3 in insol. fraction	% Cr_2O_3 in sol.	% colloidal clay[1]	% Al_2O_3 (in sol. fraction)
4.0 *N* Glycolic	0.067	0.281	0.080	0.133	5.95	3.02
FTA	0.200	0.133	0.147	0.067	6.18	2.80

1) total insolubles minus (Fe_2O_3 plus Cr_2O_3) computed as clay with 14 per cent water.

Note: Since there were 4.12 per cent Cr_2O_3 in the filtrate of the hydroxides, the total Cr_2O_3 in both tests is 4.33 per cent of which less than 5 per cent was retained by the two precipitates.

Experimental

a. Wet Oxidations

Reagents:

1. Leather oxidant[4]: 2 volumes 70 per cent c. p. perchloric to 1 vol. 80 per cent c. p. sulfuric acid, or in more convenient units: a stock solution made by first adding 200 ml. conc. sulfuric acid (95 per cent) to 70 ml. water and, after cooling, adding the 250 ml. 80 per cent sulfuric acid thus prepared to 500 ml. perchloric acid.
2. Conc. c. p. nitric acid
3. 0.03 per cent potassium permanganate solution (0.3 g / 1 c. p. $KMnO_4$)
4. 1.5 *N* HCl (=1 vol. conc. c.p. hydrochloric acid to 7 volumes of water)

Directions: Consult A. Küntzel[5]. However, instead of the specified one ml. HCl (1:1) the corresponding amount of 1.5 *N* acid, namely 4 ml., are added.

b. Digestions of leather with dilute acids.

Reagents:

1. 2.0 *N* H_2SO_4 (103 g. or 56 ml. per liter c.p. sulfuric acid, 95 per cent.)
2. FTA, a solution which is 1.0 *N* for formic as well as for trichloracetic acid, prepared by dissolving in water 50 g. c.p. formic acid (90 per cent) and 163.5 g c.p. CCl_3COOH and diluting to 1000 ml.
3. 4.0 *N* glycolic acid, prepared by dissolving 434 g / 1 of 70 per cent techn. glycolic acid (Eastman Org. Chem.). This solution contains 0.044 g / 1. Fe_2O_3 and 0.020 g / 1 Al_2O_3. The figures for these oxides in the soluble fraction of Table VIII have been corrected for the quantity of contaminants present in glycolic acid.
4. 2-butyloctanol (Carbide and Carbon Chem. Corp.)

Directions: Weigh out 1.5g (in the case of zirconium leather because of its high mineral content 0.5g) ground leather and boil under reflux for two hours in a 150 ml. erlenmeyer flask with 40 ml. of one of the acid solutions listed

above. Add also 1 to 2 drops of butyloctanol (or of any other neutral defoamer). Cool and filter through a suitable filter (in most cases Whatman No. 4 is satisfactory, but sometimes a finer filter is called for), wash with water and collect filtrate and wash waters in a 400 ml. beaker for evaporation to near dryness. Transfer to a 300 ml. Kjeldahl flask for the ensuing wet oxidation (see above).

c. Estimation of alum, chrome and iron in the wet oxidation solution. Reagents (in addition to some previously mentioned and the usual reagents for the iodometric determination of chrome and iron):

1. dilute ammonium hydroxide kept in polyethylene bottle (1 vol. conc. c.p. NH_3 to 3 volumes water.)
2. conc. c.p. NH_3
3. dry fusion mixture: equal parts of powdered K_2CO_3, Na_2CO_3 and $Na_2B_4O_7 \cdot 10H_2O$
4. 6.0 *N* HCl (equal vol. of water and conc. hydrochloric acid)
5. 20 per cent sodium acetate solution (200 g/l $CH_3COONa \cdot 3H_2O$)
6. 2.0 *N* sodium hydroxide (80 g/l)
7. 1.0 per cent solution of salicylic acid in methanol or ethanol
8. 4 g/l sodium versenate solution (disodium salt of ethylene dinitrilotetraacetate, Eastman Org. Chem.).

Directions: The "wet oxidized" acid solution, after the chlorine has been expelled, is cooled, transferred to a 500 ml. beaker and cautiously neutralized with conc. ammonium hydroxide. Any precipitate which might have formed is dissolved by the addition of a small quantity of 1.5 *N* HCl. Now bring up volume to at least 300 ml., add 5 g. NH_4Cl and start boiling. Add one to three NH_4OH solution until the precipitate reappears, boil 2 minutes and filter through a porous filter (f.i. Whatman No. 4), wash filter with water and ignite it in platinum crucible [6]. Cool and weigh as R_2O_3. Mix well with dry fusion mixture and heat moderately. When the fusion has melted increase heat to full strength for about 20 minutes. Dip hot crucible in water to dissolve melt. Remove and rinse crucible. Heat to boiling until the melt has fully disintergrated. Cool and filter through a porous filter (Whatman No. 4) into an iodine flask. Wash with water, acidify with sulfuric acid, and titrate united filtrate and wash waters with 0.01 *N* sodium thiosulfate for chrome. Rince filter with 15–20 ml. 6.0 *N* HCl, receive them and subsequent hot wash waters in a second iodine flask, add KI solution and titrate with 0.01 *N* sodium thiosulfate to obtain iron oxide.

$$1 \text{ ml } 0.01\ N \text{ thiosulfate} = 0.0008 \text{g } Fe_2O_3.$$

When larger amounts of iron are present, allow the acid to dissolve all of it on the filter before starting to wash with water and titrate with 0.1 *N* sodium thiosulfate [7]. This method suffers somewhat in accuracy from the fact that the blue iodine starch color returns in a few seconds after the endpoint has

been reached. Therefore it was superseded in the latter part of the work by titration with Versenate solution [8].

Adjust the Fe solution containing 20 ml 6.0 *N* HCl (from dissolving the precipitate) to pH 2–3 with 20 ml. of a 20% sodium acetate solution and 50 ml. of a 80g/l NaOH solution. Keep electrodes of pH machine immersed while adding alkali and stop when pH has risen over 2.0. Add a few drops of a 1% alcoholic solution of salicylic acid and titrate with 4 g/l sodium versenate solution to colorless.

d. Determination of Zirconium

Reagents:

1. 40 g/l hydroxyphenylarsonic acid (Eastman Org. Chemicals)
2. Wash solution, consisting of 5 g hydroxyphenylarsonic acid and of 8.5 ml. conc. HCl per liter. (This quantity of HCl makes a 0.25 *N* solution).
3. 30 per cent of hydrogen peroxide
4. 3.0 *N* sulfuric acid (84 ml. c.p. conc. sulfuric acid per liter)

Directions: Consult Somerville & Wendkos [9] or the original study by Simpson & Chandler [10]. The total acid concentration of a "wet oxidized" solution after dilution to 200 ml. is about 1.0 *N* and thus well below the maximum concentration of 1.8 *N* sulfuric acid which these authors hold to be permissible.

When Zr is to be determined in the ash of leather, it is fused (see above) and dissolved with 3.0 *N* sulfuric acid, filtered if necessary, and precipitated with hydroxyphenylarsonic acid. When TiO_2 is also present, it is kept in solution by the addition of 15 ml. 30 per cent peroxide solution. As shown above, this may be necessary in the fusion as well as in the wet oxidation method. However, when glycolic acid is used for the digestion of leather, Ti from titanium pigments is not found in the soluble fraction which contains the Zr.

e. Determination of Zinc Sulfide

Reagents:

1. 5 per cent formaldehyde solution (50 g/l c.p. formaldehyde in water)
2. 20 per cent citric acid solution (200 g/l c.p. citric acid)
3. Conc. c.p. NH_3
4. 5 per cent sodium sulfide solution (50 g/l filtered $Na_2S.9H_2O$ sol., kept in polythene bottle)
5. Methyl red/methylene blue indicator.

Directions: For the determination of zinc in the soluble fraction obtained by digesting leather with FTA (Method b) wet oxidize as above, reduce chrome, if present, by heating to a boil with 5cc. 5 per cent formaldehyde solution, cool, filter is necessary, add 15–25 ml. 20 per cent citric acid solution and enough conc. NH_3 to turn the color of methyl red/methylene blue indi-

cator to a distinct green. Admit H_2S gas if available. However, it is simpler to use 5–10 ml. 5 per cent Na_2S or $(NH_4)_2S$ instead. The possible occlusion of Na is insignificant. After 16 hours filter the ZnS through a fine filter, wash with cold water and ignite to ZnO in a porcelain crucible.

1 mg. ZnO = 1.2 mg. ZnS.

As a check for the accuracy of the acidic digestion a leather charge of 1.0 g. was wet oxidized, filtered and the filtrate analyzed for Zn in the manner described above.

5. Summary

A study has been conducted with the goal of developing a systematic analysis for all kinds of mineral leather, i. e., a method of analysis which allows to determine the mineral tanning agents without interference by inorganic pigments and fillers. It has been shown that an organic acid mixture, and in a special case a strong solution of a hydroxyacid, are best suited to this purpose.

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Tanning with Melamine and Formaldehyde

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Introduction

Methylolmelamines have been in use for tanning for some time, mainly in conjunction with alum, or as a retannage of chrome, for white leather. Daw-

son [1] showed that a preparation made by heating a solution of approximately three and one-half moles of formaldehyde and one mole of melamine possessed tanning properties. The resulting monomeric methylolmelamines can be used in this form or isolated as a crystalline product. Niedercorn and Thayer [2] showed that a mixture of melamine and paraformaldehyde can be reacted in the same way. Such a mixture must be dissolved and reacted in hot water by the tanner, to decompose the paraformaldehyde and form the monomer before use as a tanning agent. Niedercorn [3] has discussed the procedure for the use of these products.

It has been found that free melamine and free formaldehyde can be used for tanning [4]. It is not necessary to dissolve and react them prior to use. The melamine is entered through the head of the drum and dissolves gradually at room temperature as it reacts with the formaldehyde.

This procedure is convenient for several reasons. The disagreeable and time consuming operation of heating a solution of formaldehyde is avoided. No polymerization of the monomer can take place before tanning and there is no solution which must be used promptly. The limited solubility of the melamine provides an automatic regulator of the rate of tanning and yet the solubility is adequate to permit tanning in the normal time. When melamine is used on pickled skins the alkalinity is often sufficient to act as a depickling agent and the pH is controlled within the range of 4.0 to 5.0 for tanning and fatliquoring [5]. Chronologically, the research on tanning with melamine and formaldehyde preceeded the work with resorcinol. Such a method of tanning has two fundamental advantages. First the basic and more economical raw materials are used. Second, the tanner controls the method of tanning, so that different results can be produced by varying the ratio of formaldehyde to melamine or resorcinol.

Possibly the first published attempt to use a solution of monomers for a polymeric tannage was made by Porter [6], who reacted urea and formaldehyde and then used the solution for tanning. Examples were repeated under various conditions. Also urea and formaldehyde were added directly to the tanning liquor and the monomer allowed to form in the presence of the skins. The leather resembled a formaldehyde tannage. Run under conditions similar to the melamine tannage, the shrink test was lower than that obtained with the same amount of formaldehyde alone. Thiourea was also tried with negative results.

Procedure

Raw Stock Pickled goatskins, rebrined, horsed and drained overnight.

Formula

Skins, drained pickle weight	50 lbs.
Water @ 80 F.	5 gals.

Salt	2.5 lbs.	
Run 15 min. pH 2.5		
Melamine	2.5 lbs.	5%
Run 30 min. pH 5.9		
Formaldehyde (36% by weight)	5 lbs.	10%
Run 3 hrs. pH 4.7 Shrink test 166°F.		
Temp. of liquor 82°F.		
Run 6 hours more and shut down overnight.		

Next Day

Run 15 min. pH 4.3 Shrink test 194°F.
Washed and fatliqured

Theoretical

It is apparent that there is a strong possibility of the reaction of the methylol groups in trimethylolmelamine with the free amino groups in collagen with the elimination of water. This would form a covalent bond whose high strength would account for the fact that leather which does not shrink in boiling water can be obtained readily by the use of an adequate amount of melamine and formaldehyde. It is therefore probable that this is another example of the Mannich reaction[2] taking place in tanning. The Mannich reaction has already been discussed fully in connection with the mechanism of tanning with resorcinol and formaldehyde[3]. The only unusual features in the case of melamine are that the active hydrogen atoms are supplied by amino groups and strong acid is not required.

The three methylol groups of trimethylolmelamine can react to form a three-dimensional polymer or cross-link with polypeptide chains for multipoint fixation. The high degree of cross-linking with the protein and the properties of a three-dimensional polymer are responsible for the low tensile strength of the leather. This can be controlled by lowering the ratio of formaldehyde to melamine or more economically by lowering the amount of melamine to keep the shrink test within the range of 190 – 200°F. Combination tannages, using limited amounts of melamine, produce the same effect.

Summary

An *in situ* tannage with melamine and formaldehyde has been described. A mechanism of tanning based upon the Mannich reaction has been postulated.

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ABSTRACTS

Effects of Lubrication on Stitch Tear Strength of Chrome Retan Leather. By S. G. Shuttleworth. *J. Soc. Leather Trades' Chemists* **37**, 2 (1953). The main disadvantage of chrome retan leather is its tendency to poor stitch tear strength, a disadvantage which might be offset by its ability to hold more lubricant than straight chrome leather without surface greasiness. These experiments were designed to show the differences in effects of various quantities and types of fat liquors, and a drum stuffing mixture, and differences between skin types. By simultaneous fatliquoring of goat, calf and sheepskins in the same drum it was hoped to find indications of the lubricants which minimized butt to belly variations in fat uptake. The skins were chrome tanned followed by retannage with bisulfited wattle, the total time of both chrome and wattle tannage being three (3) hours. Comparisons were arranged between skins divided down the backbone after tanning and prior to fatliquoring in order to eliminate between the skins variation errors. Only identical sampling positions from mated half skins were compared. The following fatliquors were used. Two parts whale oil and one part sulfonated whale. One part whale oil and two parts sulfonated whale. Two parts sperm oil and one part sulfonated cod. Two parts neatsfoot oils and one part sulfonated cod. One part wool grease, one part mineral oil and one part sulfonated cod. Drum stuffing with five parts wool grease, three parts whale oil and two parts neatsfoot oil. The sulfonated whale oil analysed as 3.7 percent SO_3, 88.3 percent total active ingredients and 83.6 percent fatty matter: the sulfonated cod 3.4 percent SO_3, 75.7 percent total active ingredients and 71.4 percent fatty matter. Examination of the leathers resulted in the following general conclusions. No significant differences were found in the ratio of oil increase to oil added between the five different fatliquors. At the 3 percent level of fatliquoring, the loose textured sheepskins absorbed fatliquor at the expense of the goat and calfskins. This was not apparent at higher levels of fatliquoring, nor with the drum stuffing mixture. Fatliquor was satisfactory up to the addition of 9 percent on damp shaved weight, but poor after that. The uptake of the drum stuffing mixture was less efficient, but this was probably due to the inability to simulate good practical conditions on a pilot plant scale. Drum stuffing gave a more uniform uptake on the various skin types indicating that it is less likely to emphasize the relative looseness of texture of a mixed pack of skins or bellies compared with butts. No significant differences were found between the ratio of stitch tear test increments to oil increments when comparing the various fatliquors and the drum stuffing mixture at any of the levels used on any of the types of skins used. The goatskins and calfskins derived more benefit from fatliquoring than the sheepskins, possibly due to the higher natural fat content of the latter. The initial addition of fatliquor (3 percent) produced the greatest effect on the strength, and the sheepskins derived little benefit beyond the 6 percent level of fatliquoring. More than 6 percent of fatliquor gave greasy results with whale oil, sperm oil and wool grease fatliquors. Neatsfoot plus sulfonated cod gave greasy results with 12 percent fatliquors. Both stuffing experiments gave greasy results. Samples taken parallel to the backbone gave considerably higher tear strengths

than samples taken perpendicular, but there were no significant differences between grain to flesh or flesh to grain directions of stitch tear. The goatskins were considerably stronger in stitch tear strength than the calfskins or sheepskins. The two latter were about equal in strength. R.H.T

The Architecture of the Collagen Fibrils in Pelt as Revealed by the Electron Microscope. D. Burton and R. Reed. *J. Soc. Leather Trades' Chemists* **37,** 13 (1953). The present picture of the architecture of collagen is vague, largely because of lack of data and the fact that different units of measurement have been used. The corium, according to electron microscopists, has fibrous structure falling into four categories, (1) fibers 30,000-2 000,000 angstroms in thickness, (2) fibers 10,000-30,000 angstroms in thickness, (3) unit fibrils of indefinite length but uniform thickness for any particular skin and from which the first two are elaborated and (4) fine filaments from which the fibrils are elaborated. Finally there are the molecular chains of collagen from which all these fibrous systems are built. Important to the tanner is the fact that all skin collagen is composed of striated unit fibrils of uniform width and indefinitely great length, a structure which probably must be maintained throughout all stages of leather making. By calculation 19,000 molecular chains could be accomodated in one unit fibril. The cross striations are often in perfect alignment. They are visible under the electron microscope only in the dry state. Some observations have indicated that the dark band is more extensible than the light. If true this would indicate that collagen is capable of extension at the fibril level although it is known to be virtually inextensible at the microscopic level. The reason why collagen fibrils possess bands is unknown. Banding may be a mechanism unique to collagen fibrils whereby their lateral cohesion, when forming part of a body organ, is controlled. The configuration of the collagen polypeptide chain is unknown but is undoubtedly unique. According to a recently proposed collagen model, which seems to fit most of the known facts, the carboxyl group is in a planar arrangement so arranged that hydrogen bondings with side chain groups are possible. These workers consider that the polypeptide chains join in sheet structures stabilized by the hydrogen bonding. Bands are explained as folds within the length of the collagen molecule taken as 640 angstroms long. At the present state of knowledge reticulin may perhaps be best regarded as a form of collagen which holds the fibrils of the collagen fiber together. Studies of elastic tissue fibers have mostly been made on the ligumentum nuchae of the ox and the aortic meedia of man. Elastase breaks down the fibers to fibrils which are finally reduced to corpuscles. The fibers consist of a system of fibrils bound together with a dense cementing substance. When treated with alkali, such as lime water, the tissue loses stability becoming easily soluble in many solvents. So liming should loosen such fibers. The material between fibers constitutes about 10 percent of the dry weight of freshly flayed skin. Little is known about it but it may be of importance in making leather, since liming undoubtedly affects it. As a result collagen ready for bating and tanning may be greatly different from native collagen. Collagen fibrils must not be broken down to filaments because this is irreversible degradation. Ten percent of sodium chloride in green salted skins and curing mixtures prevents this filamentation. In soaking, sodium chloride causes splitting of the fibers, prevents filamentation and helps loosen interfiber material. The effect of other salts needs study. Highly alkaline soaks cause filamentation. Liming carries splitting of the fibers further. Usual liming does not appear to affect the cohesion of the filaments within the fiber. It does alter fiber to fiber cohesion. Mucoprotein links are ruptured altering the physico-chemical properties of the fibrils. If carried too far liming causes degradation through filamentation. Caustic soda causes degradation more easily and is therefore too harsh. Bating completes removal of the interfiber debris

and, because filamented fibrils are digested, removes any damaged fibrils. Thus it is essentially a cleaning process leaving only intact fibrils. Obviously, if there is any appreciable filamentation developed during curing, soaking or liming, there will be a proportionate loss of hide substance during bating. Acids used for pickling will cause filamentation unless prevented by the presence of sodium chloride. Other salts may increase or decrease filamentation. The concentration of acid is significant. Hydrochloric acid causes filamentation in tenth normal but not in normal solutions. Acetic acid causes filamentation at both concentrations. As a summation, a fresh hide is visualized as consisting of collagen fibers, unit fibrils and filaments. The electron microscope shows that the fibers vary in width and thus the distance between them varies. They are not straight but interwoven in three dimensions. The unit fibrils are of uniform thickness and can be split into filaments. The whole structure, which is of complex and irregular weave, includes elastic tissue and reticulin fibers (an immature form of collagen) which are bound together by a dense mucoid material. In preparing the skin for tanning it is important that the structure should be loosened by removal of interfiber material and splitting of large into smaller fibers, then cleaned up by removal of interfiber material. It is vital that the process does not go so far as to materially split fibrils into filaments. Whether tanning particles can reach all collagen fibril units depends upon how thoroughly the loosening of fibers has been carried out. R.H.T.

Standardization of Leather Bates. E. Lenk and H. S. Owen. *J. Soc. Leather Trades' Chemists* **37,** 22 (1953). It is generally accepted that bating property runs parallel to the digestive power as measured on casein or gelatin in the laboratory under similar conditions of time, temperature and pH. The authors found it difficult to obtain reproductable results by the Lohlein-Volhard method as modified by Kuntzel. This led to an investigation into the possibility of preparing a product of standard enzymatic activity with which all leather bates can be compared. Chlorides and sulfates of ammonia and sodium do not activitate the proteolytic enzymes but do bring them into solution and so greatly enhance their digestive action. Casein is used as the substrate. Since even in its purest form, as prepard by Hammersten's method, it always has some peptones which are not precipitated by acid, it is necessary to know the exact amount precipitable in the casein being used. This is accomplished by determining the total nitrogen (Kjeldahl method) and the nitrogen in the filtrate from the casein solution precipitated by 0.1 *N* HCl containing 5 percent anhydrous sodium sulfate. Total nitrogen minus the nitrogen in the filtrate is the available nitrogen. The activity of an enzyme must be expressed in the amount of available nitrogen broken down. It was determined that, within the range of available nitrogen equivalent to 3-5 percent casein, the amount of nitrogen digested is independent of the concentration of the substrate. Also digestion is proportional to the amount of enzymate used up to 30 percent breakdown of the substrate. The Lohlein-Volhard method, as modified by Kuntzel, is described in full. The authors consider it unsatisfactory because, (1) it does not take into account the variable nitrogen content of different caseins, (2) the small weights of leather bates used (0.1 to 0.4 g.) cause sampling errors to be large and (3) the use of alpha naphthothalein indicator throws the titration end point into the 7.3-8.7 pH range. An indicator is preferable which changes at pH 6.5-7.0. Lenk's modification uses bromthymol blue as the indicator. It was decided that the best procedure is to select a standard enzymate and to determine the weight of the unknown having the same activity. Fifty ml. of a solution prepared by dissolving 1 g. of the standard enzymate and 8 g. of ammonium sulfate or sodium chloride in one liter of water (i.e. 50 mgm. of the standard enzymate) will digest 25 mgm. of available nitrogen in a 5 percent casein solution at pH 8.2 in 1 hour at 40°C. Since 1 g. of the standard would dissolve 500 mgm. of nitrogen it

is said to have 500 trypsin units (T. U.). The method for preparing and standardizing the enzymate is described. The procedure calls for using an enzymate of greater than standard strength and, after determining the exact strength, diluting to standard strength with wood flour. The salts are not added to the standard but are added when the bate is made. Such a standard enzymate, if not over 10 percent in moisture content, will keep in air tight bottles for many years. In determining the strength of an unknown a series of different weights is used and the amount of 0.1 *N* NaOH required for titration after digestion plotted against the mgm. of the unknown used. This will plot as a straight line because the process is carried out at below 30 percent break down of the substrate. The ml. of 0.1 *N* NaOH required for the standard is also determined. A line is drawn at this number of ml. parallel to the mgm. used. At the point where this line intersects the unknown curve a line is dropped to the mgm. used line giving the mgm. required to be equivalent to the 50 mgm. of the standard used. In an example given the weight of the unknown required was 148 mgm. The strength of this unknown is $500 \times 50/148 = 169$ trypsin units. Incubation is at 40°C. for 1 hour. The authors maintain that ½ hour at 50°C. will give identical results. R.H.T.

The Reactivity of Protein in Fibers: Some Analogies Between Keratin and Collagen. By J. B. Speakman. *J. Soc. Leather Trades' Chemists*, **37**, 37 (1953). Comparison of the amino acids present in collagen and keratin from wool are given in a table. The alkali titration curves of the two proteins differ because of the reaction of cystine and cysteine in the case of keratin, but there is close similarity between the acid titration curves. Wool keratin gives widely differing curves with different acids. The reasons for this are discussed and a means given for calculating the internal pH of the wool fiber is given. Using the corrected pH values obtained in this manner hydrochloric and sulfuric acids, for example, give similar curves although they vary widely when using the experimental pH values. The curves from the calculated values are termed "true" titration curves. It is believed that extension of this procedure to collagen will be instructive. Neutral salts, of the nature of KCl in solution, seem to cause a slight increase in resistance to extension of wool fibers. However the extension is considerably less than is caused by the relative humidity of the atmosphere above similar KCl solutions when the wool fibers are exposed to such atmospheres. By plotting the differences between the two resistances it is deduced that KCl has a pronounced weakening effect upon the fibers. Lithium bromide, an example of salts capable of breaking hydrogen bonds, causes such a great weakening effect that it overbalances the strengthening R.H. effect up to 7.8 molar concentration. The molecular structure of keratin is stabilized by salt linkages, hydrogen bonds and cystine linkages between neighboring chains, supplemented by Vander Waal's forces. As the cystine linkages are absent in collagen its stability, particularly the hydrothermal stability, is less than that of keratin. Keratin is undoubtedly cross linked by treatment with formaldehyde, benzoquinone and basic chromium acetate. In the first two cases the fibers show an increased resistance to deformation. There can be little doubt that similar reactions will occur with collagen. Factors of fundamental importance in the theory of practical tanning are the extent to which the protein structure is accessible to the reagent and the distance between groups to be bridged. It is known that high polymers in general consist of ordered (crystalline) and disordered (amorphous) regions. As the latter are much more accessible than the former, a knowledge of their proportions is of importance to the study of reactivity. Two methods for determining the crystalline/amorphous ratio for wool keratin are given. These methods should be applicable to collagen. Regarding the distance between groups to be bridged, collagen, which swells considerably, allows intermicellar reactions through the use of polyfunctional compounds such

as lignosulfonic acid and basic chromium sulfate. For intramicellar reactions, especially for keratin where swelling is slight, it is necessary to form polymers *in situ* from monomers of low molecular weight. Impregnatuon with ferrous ammonium sulfate followed by treatment with hydrogen peroxide, for the creation of hydroxyl radicals, and then with methacrylic acid as the monomer to be polymerized, is given as an example. Processes of this kind should have practical applications in leather manufacturing especially as the polymer deposited, in appropriate cases, may be followed by cross linkage. The general conclusion is that workers in wool and leather have much in common and collaboration is therefore desirable. R.H.T.

Stitch Tear Tests on Vegetable Tanned Leather. By F. G. Mitton. *J. Soc. Leather Trades' Chemists*, **37**, 53 (1953). The experimental work described in this paper was confined to firm leather only, and to stitches made some distance from the edges of the specimens. The method of test, leather used, variation factors, statistical plan and preparation of the specimens are fully described. Four thicknesses: 2.21, 4.42, 6.63 and 8.84 mm. are used. Also there were four distances between holes, 3.0, 6.0, 9.0 and 12.0 mm. All holes were bored and were either 0.04 or 0.08 inches in diameter. Two wires with diameters 0.036 and 0.022 inches respectively were used. The results obtained are very well visually summarized by two figures. In one figure distance between holes is plotted against tearing load in pounds. In the other thickness versus tearing load is shown. In both cases the figures are double showing comparisons between the two sizes of wire used. In the distance between hole vs. load figure, curves for all four thicknesses are shown. In the thickness vs. load figure, curves for all four distances between holes are plotted. The experimental results show that the process of rupture of a compact leather in a stitch tear test is complex, and that the breakdown may in some circumstances be dominated by the cutting action of the wire or thread used in tests, while in other circumstances this cutting action may be relatively unimportant. Whether it is or is not important depends upon the thickness of the leather and the distance apart of the holes, and the dependence of the tearing load upon these factors is therefore correspondingly complex. In consequence stitch tear tests are unlikely to be of any value for comparing different leathers unless the conditions of test (as regarding thickness and hole distance) correspond closely with those in which the leathers are to be used. Since load is not even approximately proportional to thickness, it would be highly misleading to give the results of such tests as load per unit thickness, as suggested in *U. S. Federal Specification KK-L-311. Method 246.2, Superintendent of Documents, Washington, D. C. (1945)*. Other factors such as diameter of holes and diameter of stitching material are of less importance. It is shown in this work that increasing the diameter of the wire raises the tearing load, and that increasing the diameter of the bored holes also causes a small rise of load. The dependence of the load upon thickness and distance apart of the holes is complex. The load is directly proportional to the distance between holes for small distances and is the same for all thicknesses; but for larger distances the load depends upon thickness and is not proportional to the distance between holes. If the distance between holes is less than 6 mm. and thickness is small, the tearing load increases rapidly with increase in thickness. At the greater thicknesses, the load is independent of the thickness. An explanation of these observations is given. In certain circumstances the wire cuts through the fibers, and the tearing load is determined solely by the resistance of the leather to the cutting action. In other circumstances the wire causes bending and rupture of the "bridge" as a whole.
R.H.T.

An Electrometric Method for the Determination of Relative Opacities of Water Pigment Finishes. By J. S. Mudd and F. E. Downs. *J. Soc. Leather Trades' Chemists.*

37, 67 (1953). The desirability of having an absolutely opaque film on finished leather for the purpose of concealing marks or defects is unquestioned. Unfortunately previously existing methods and equipment for measuring opacity require a high degree of manipulative skill and visual acuteness for reasonably satisfactory results. This paper describes an apparatus and method designed to eliminate, in so far as possible, the human errors and yet give uniformly reproducible results. Light from a 6 volt bulb is collimated and directed through a control hole in a barrier type photo-cell, then through an optical glass cell containing a dispersion of the required finish and falls on a standard white surface arranged in a slide so that it can be replaced by a standard black surface. Light reflected by either surface can again pass through the glass cell to be collected by the photo-cell and subsequently recorded. The standards are arranged so that a zero reading is recorded with the black when the standard white, with distilled water in the cell, records 100. With the instrument so calibrated any finish will fall on a scale between zero and 100. A 0.5 per cent dispersion seems to produce a film comparable to a satisfactory dry film. Using the dispersion has the great advantage of being exactly reproducible, which is nearly impossible to accomplish with dry films. A table of nine finishes is given showing a range from 31 to 100. The instrument and method give reliable results on determinations of relative opacities of water pigment finishes, or similar products, without requiring a high degree of skill or judgment on the part of the operator. R. H. T.

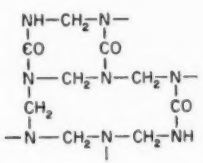
Syntans and Newer Tanning Methods. Two-Minute Tanning. P. S. Chen. *The Leather Manufacturer* **63,** No. 3, 9 (1952). Conventional tanning methods are slow because water bound to the hide makes it virtually a protein jelly impervious to both liquid and air flow. By removing the water, or otherwise destroying the jelly formation, rapid tanning becomes possible. Water may be removed by extraction with an organic solvent such as methanol or acetone. A piece of hide, dehydrated in this manner, is cut to fit a Buchner funnel placed in a suction flask. Vacuum is applied and a 5 percent methanol soluble tanning agent is poured over the disc. The tannin solution is followed by a methanol wash. Hide can be well tanned in this manner in two minutes. Another method is to remove the bound water by means of a pretanning agent such as a naphthalene syntan, which replaces the water because of its greater affinity for the hyde. The pretanned hide is then treated with an aqueous vegetable tanning liquor with the aid of vacuum as described. By using a filtered clear tanning agent of high fixation value such as cutch, placing the hide disc flesh side up, prewarming the disc by drawing warm water (50°C) through it, using tan liquor at the same temperature and regulating the vacuum so as to allow time for the pretanned hide and tanning agent to react, tanning can be accomplished in about 5 minutes. This latter method may also be used to fill lightly tanned leathers. R.H.T.

Advantages and Disadvantages of Masked Chrome Salts for the Tannage of Box and Velour Leathers. By G. Otto. *Rev. Tech. Inds. Cuir.* **42,** 181 (1950). Studies by the author confirm the findings of Stiasny and of Küntzel that the use of masked chrome liquors, while giving a finer grain and fuller leather, results in a diminished affinity for acid and direct dyes, due to the tendency to form anionic complexes. Where the liquor is glucose-reduced, the difficulty of obtaining uniformity between batches is pointed out. Dye absorption tests with leathers tanned with cationic chrome-sulfate and with non-ionized sulfito-chrome complexes show that, as the pH of the bath increases, the absorption of acid dye (orange II) decreases for both tannages, with the sulfito-leather absorbing less initially and falling off more rapidly. On the other hand, a basic dye (Methyl Violet B) is

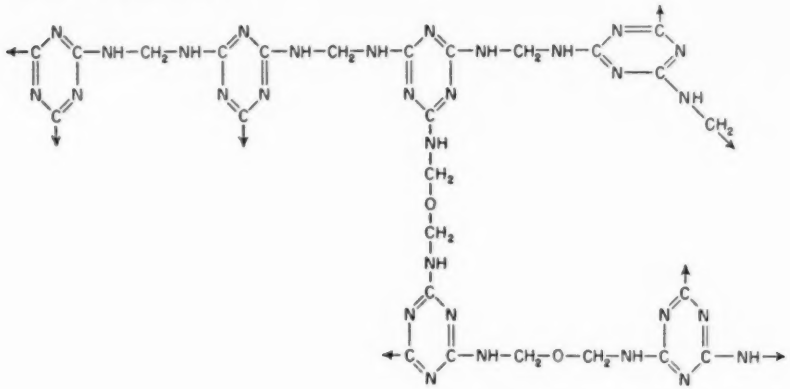
not absorbed by the cationic sulfate leather at any pH (3.5-6.5) but is increasingly absorbed by the sulfito-leather as the pH rises. Leather was then tanned with the tetra-oxalato-diol-chromiate described by Gustavson [(J.A.L.C.A. **42**, 201 (1947)] and absorption tests made with the same dyes. With Orange II, there was only 15 per cent absorption at pH 3.5 (against 99 per cent absorption by cationic sulfate leather); 4 per cent at pH 4.5, zero per cent at pH 6.0; with Methyl Violet-B, absorption increased from 58 per cent at pH 3.5 to 93 per cent at pH 6.5. It is said to be characteristic of masked chrome salts to be absorbed more slowly than the cationic sulfates and that while moderate masking gives fullness and feel, over-masking can be harmful. The tanning effect of masked Cr liquors varies with the age and the type of anion. For masking, the formiato-oxalato-, and sulfophthalato-complexes are particularly desirable, the last being always used in the early stages of tanning. For grain leathers, the usual glucose-reduced liquor can be used, combining with it an unmasked liquor during the second half of the tannage: or, first pickle with formic or sulfo-phthalic acids, followed with a tannage of cationic Cr sulfate whose basicity is increased towards the end of the tannage by small additions of phthalates or sulfites combined with adipates. Such a masking, while increasing the size of the tanning molecules, and giving fullness, scarcely affects dye absorption and has a levelling action. Such masking agents have a similar action on vegetable retannage. For tanning chrome velours, where fineness of grain is not important but where acid and direct dyes must be used for full and deep dyeing, as much cationic chrome sulphate is used as possible. By repetitive tannages with neutralization between each, up to 26.8 per cent Cr_2O_3 can be fixed. In such high chrome leathers the fibers are well separated and the structure compact, which is desirable. For general purposes, it is suggested that stock for velours should first be tanned with a mixture (equivalent to 2 per cent Cr_2O_3) of a glucose-reduced liquor and one partially masked with sodium phthalate. Neutralize with 2 per cent ammonium bicarbonate and follow with a purely cationic liquor (4 per cent Cr_2O_3), at 40°C. Again neutralize. Chrome gloving leathers, like velour leathers, should be dried before cleansing and dyeing. As this drying stabilizes anionic complexes and diminishes the affinity for the usual dyes, the totally masked liquors, which would be suitable for box, should not be used. Attention is drawn to the sulfophthalates of chrome obtained by tanning in the pickle bath prepared with sulfophthalic acid. While requiring a little more time for tannage the leather is supple, full and fine-grained. A.N.K.

Tannage Without Tannin. By P. Saint-Priest. *Rev. Tech. Inds. Cuir.* **42**, 187 (1950). The second of two papers on this subject [see abstract *This Journal*, **48**, 112 (1953)]. The factors studied were: (1) Lengthening of the polymerization time by inhibitors. (2) Use of dispersing agents. (3) Elimination of part of the active groups of the mono- or polymers, (4) Dilation of the mesh of the condensation network. (1) *Increase of polymerization time;* sulfur and sulfur derivatives not only increase the resistance of the urea-formaldehyde resins to water and acids but also improve their elasticity. In this last, they appear to act as negative catalysts in all resins whose monomers contain methylol groups. Since thiourea is expensive, H_2S and thioformaldehyde $H_2S.2HCHO$) were tried. Also tried were the alkaline sulfides or polysulfides, polythionates, thiosulfates, even colloidal sulfur. For satisfactory tannage, from 1.0 to 1.5 per cent of sulfur was sufficient larger amounts giving poorer leather. However, the use of even 0.5 per cent sulfur increases the time required to reach the zone of usefulness to 200 hours and it is concluded that, while the tests confirm the hypothesis of the effect of sulfur on this type of resin, the process is not practical. (2) *Use of dispersing substances.* This phase was approached from the point of view of the production of uncrushable fabrics in which treatment with urea-formaldehyde resins, while achieving uncrushability, causes a certain stiffness due to

the formation of a continuous film of resin on the fibres. This stiffness can be overcome by using resins containing independent elements or by the use of certain colloids added at the time of treatment. Variation of the proporation of urea to HCHO was therefore tried. An excess of urea leads to formation of methylene compounds which react rapidly to give insoluble resins while an excess of HCHO leads to stable syrups which do not precipitate. An increase in urea, by accelerating precipitation reactions should lead to a discontinuous film. In practice, the hard zone was considerably retarded and tannage speeded but no definite end to the condensation was achieved, and the leathers were less supple. Simultaneous impregnation with dimethylolurea and aluminum salts was tried but led to no practical result. (3) *Elimination of active groups.* When dimethylolurea condenses with alcohols, the rigid, three-dimensional structure is modified by the formation of mono- or di- ethers and this reaction is used in varnish formulation. However, one American patent suggests them as tanning agents. Such resins lead to leathers of good suppleness. However, in order to remain within the zone of usefulness, the proportion of dimethylolurea inhibitor must be set exactly. Too great a quantity of alcohol stops the reaction in the hard zone while too little will allow it to pass through the zone of usefulness and re-enter the hard zone. Solubility of the resins in the alcohol leads to difficulties and it is found best to treat the white hide in an aqueous solution or dispersion of the monomolecular components which, after complete inhibition, are either self-resinifying or resinify by catalysis. Under these conditions, the resin forms between, and isolates the fibrils and leads to a true tannage. Careful drying is indicated so that the solvent evaporates as the polymer forms and deposits. Substances other than alcohols can be used in this manner. Examination of the residual tanning liquor is a useful, if empirical, guide as to the tanning power of a dimethylolurea auxiliary substance system. While the liquor should contain the least possible amount of precipitate, sufficient is always present to study its appearance and judge the tannage proceeding therefrom. There are five principal forms: (A) Very fine methylene ppts. These are powdery, harden with time and, on drying, yield very hard masses. In this group belong the tannages with unmodified dimethylolurea. (B) Methylene ppts. in association. These do not harden much but, on drying, give very firm granules. In this group belongs dimethylolurea associated with dispersing substances. (C) Pasty methylene ppts. These correspond to polymers "blocked" by alcohols and only appear when a relatively high percentage of modifier (e.g 5 per cent EtOH) is used. (D) Flocculent methylene ppts. These are rarely met with except on condensation of dimethylolurea with synthetic or vegetable tannins, which harden a little on drying. Also those of mono- or polyphenolic compounds which only alter slightly. (E) Fibrous ppts. These indicate ideal conditions. They are insoluble in the medium, do not change, and have a peculiar character. On drying, no modification takes place and the fibers are very supple. In this group belong the condensation products of dimethylolurea with modifying agents which eliminate reactive groups. (F) No ppt. is obtained. This is the case when the auxiliary substance is a solvent for the resin and is characterized by the lack of tannage unless a preliminary drying is given. (4) *Dilation of the network.* While dimethylolureas give closed networks of the type:



the methylolmelamines give:



and, while the urea-formaldehydes must be restrained during polymerisation, the methylolmelamines can act freely while still leading to supple leathers. By introducing into the urea-formaldehyde system linear or cyclic compounds having two or more formaldehyde-reactive groups, polymers can be obtained which simulate the behaviours of the more expensive methylolmelamines. For example, certain syntans can be used in this manner. In such cases, the first hard zone practically disappears while the zone of usefulness is considerably extended, and tannage is very rapid. It is pointed out that tannage with methylol resins divides itself into two possibilities, (a) Use of methylolmelamines, which are costly but relatively easy to apply. (b) Use of modified dimethylolureas, which are much cheaper but more difficult to use. In conclusion, the authors indicate several types of leather on which this latter type of tannage can be applied. A table is also given summarizing the various types of modification and indicating the characteristics of the resultant leathers. A. N. K.

The Conversion of Collagen to Gelatin and Their Molecular Structure. By W. M. Ames. *J. Sci. Food Agr.* **3**, 454 (1952). Through *Chem. Abst.* **47**, 3020 (1953). The effect of the use of acid or alkali in the manufacture and subsequent heat-treatment on the properties of gelatin was studied. Isoelectric point (IEP), taken as the pH value of maximum opalescence is expressed in terms of the quantity of standard acid or alkali required to bring a gelatin solution, previously neutralized to the phenolphthalein end point, to the IEP, sometimes without stating the pH value. Experiments with pig skin, rabbit skin, ox sinew, and ossein showed that the IEP of gelatin is independent of the collagen source, but is dependent on whether the collagen is treated with calcium hydroxide or hydrochloride acid prior to conversion into gelatin. The IEP values of alkali-prepared gelatin (I) and acid-prepared gelatin (II) were 4.75-5.27 and 8.0, respectively. When I was prepared by liming collagen for 0 to 43 days prior to cooking, the IEP of I declined with increasing time of liming from pH 5.46 to 4.75; formal titration (ml. 0.1 *N* NaOH per g.) increased from 3.23 to 4.01; jelly strength increased from 86 to 182; rate of conversion increased from 6 to 37 g. per hour. Percentages of N in ox sinew, II and I were 18.49, 18.52 and 18.08-18.15, respectively. The loss of N during preparation of I agreed well with the shift of IEP. The IEP of collagen (taken as the point of minimum swelling) shifted

from pH 7.8 to 4.8 after liming. On heating untreated ox sinew, limed ox sinew, and I in H_2O at pH 8 for 6-7 hours, at 80°, N losses were 0.49, 0.03, and 0.08-0.17 percent of total dissolved N, respectively. On heating I at 95° at pH 10, the IEP was shifted from pH 4.83 to 4.74, with a small loss of N, while when I was heated at pH 4.83, the IEP was shifted to pH 4.97, presumably owing to loss of CO_2. When II was heated at pH 10.4, the IEP shifted from pH 8.1 to 5.4, with loss of 0.3 percent NH_3, and the product showed extensive degradation. When II was heated at pH 4.5-4.9, the pH value of the solution increased by about 0.1 pH unit; the IEP (by titration to maximum opalescence) dropped from pH 8.1 to 6.55, but the IEP determined by the ion-exchange method rose from 8.1 to 8.25. The formal titration of I was unchanged by heating at pH 4.75, and was increased from 3.92 to 4.24 by heating at pH 10.4. The formal titration of II was unchanged by heating at pH 10.4, and increased from 3.59 to 3.79 on heating at pH 4.9. The slight changes in formal titration indicate that thermal degradation of gelatin is not accompanied by an increase in terminal amino groups. Molecular models are proposed for collagen, which involve two types of cross-linkages between polypeptide chains, or, alternately, two types of bonds within single chains, one type being broken readily by alkali and the other by acid.

Effect of Preliminary Treatment of Hide on Action of Enzymes. By I. S. Shestakova. *Legkaya Prom.* **9**, No. 2, 13 (1949). Through *Chem. Abst.* **47**, 1959 (1953). Trypsin does not act on untreated collagen. Acids and alkali create conditions favorable for the action of enzymes. Optimum condition is produced by prolonged treatment with lime. For the same period, sulfuric acid is more effective than lime. Conditions governing action of trypsin are presence of –CO–NH–bonds accessible to the trypsin and free active groups $–NH_2$, –NH, and –OH. Trypsin and pepsin differ in their action; the former acts primarily on the bonds in the main chains and the latter primarily on the side chains.

Mechanism of Absorption and Distribution of Acid in Fur Hides During Pickling. By K. A. Krasnov. *Legkaya Prom.* **9**, No. 2, 19 (1949). Through *Chem. Abst.* **47**, 1949 (1953). Degreased wool and skin containing up to 65 per cent water were pickled at 20-22° for 15-1440 minutes in solutions containing 3.23 g. l. H_2SO_4 and having a liquid coefficient of 4. Absorption was practically complete in 45 minutes by wool and in 135 minutes by skin. Wool plus skin occupied an intermediate place. After 45 minutes the acid was desorbed when the wool was immersed in progressively weaker solutions. When the wool and then the skin were immersed in the original solution, desorption of acid by wool took place after 135 minutes, while the derma continued to absorb acid. Differences are due to differences in physical-chemical nature between keratin and collagen.

Strength of Bond of Tanning Sulfonic Acids With Collagen. By G. I. Kutyanin. *Legkaya Prom.* **9**, No. 5, 14 (1949). Through *Chem. Abst.* **47**, 1959 (1953). Sulfonic acids are joined rather firmly to collagen, as shown by the considerable amount of tannins in collagen which is not separated by soda. This interaction is apparently not only ionic but homeopolar. The most important role in bonding of collagen with aromatic sulfonic acids is the process of their condensation with HCHO or other condensing media. Interaction of sufficiently polymerized sulfonic acids with collagen differs qualitatively from interaction of non-condensed sulfonic acids. Irreversibly bound tannins in leather can be regarded as combined with both the basic and the peptides groups of the protein.

Kinetics of Chrome Tanning of Sheepskins. By K. A. Krasnov. *Legkaya Prom.* **9**, No. 5, 17 (1949). Through Chem. Abst. **47**, 1959 (1953). Four methods were used: (1) without pickling, (2) with weak pickling, (3) with moderate pickling, and (4) with strong pickling. Method (1) can be used effectively only for hides with a loose structure of the leather fabric, which requires no previous softening; this method proved best as regards rate of tanning and automatic control. Methods (2) and (3) had a smoother course than (1) and uniformity of tanning was better; both are suitable where softening is required. Method (4) required much time (12-16 hours); it is suitable for hides with a dense structure of the derma and those having bacterial damage, with weakened hair. As regards uniformity of tanning of derma and content of contraction of area, this method was best.

Sulfite Waste Liquor Tanning Agents. I. Analysis of Sulfite Waste Liquor Tanning Agents and Its Mixture with Natural Tannins. By Y. Hachihama and Y. Kyogoku. *J. Chem. Soc. Japan, Ind. Chem.* Sect. **54**, 197 (1951). Through *Chem. Abst.* **47**, 1959 (1953). Methods have been studied for the determination of lignosulfonic acid (I), the tanning agent from sulfite waste liquor, as well as for the mixture of the tanning agent and tannin. The amount of I determined as tannin by the A.L.C.A. method corresponds roughly to 70 per cent of the total I found by determining methoxyl groups. In the A.L.C.A. method the amount of absorbed I determined as the difference of the total and unabsorbed I agrees well with the amount of tannin constituent. A method of analysis is proposed for the mixture of tanning agent and natural tannin by the combined use of the A.L.C.A. method and the determination of I by means of methoxyl group determination.

The Caesalpina Species as Tanning Materials. By F. N. Howes. *Material Vegetables* **1**, 60 (1952). Through *Chem. Abst.* **47**, 1959 (1953). A review with 18 references.

Brain Tannage. By M. Shimizu and M. Kubota. *J. Chem. Soc. Japan, Ind. Chem.* Sect. **54**, 201 (1951). Through *Chem. Abst.* **47**, 1960 (1953). The action of cow brain tannage is attributed to the action of phosphatide and of the oxidized fats in the brain.

Theoretical Considerations on the Tanning Process. By J. P. van Vlimmeren. *Chem. Weekblad* **48**, 945 (1952). Through *Chem. Abst.* **47**, 1960 (1953). A review with 56 references.

Interaction of Chrome and Sulfite Cellulose Liquors in Combination Tannage. By L. P. Gaidarov. *Legkava Prom.* **9**, No. 6, 16 (1949). Through *Chem. Abst.* **47**, 1960 (1953). Mixtures are prepared from equal volumes of liquors. Experimental and calculated sp.gr. were in agreement. The color of the mixtures in reflected light varied with the concentration of one or the other material. All mixtures were turbid and gave a distinct Tyndall cone. Precipitates were observed. They consisted entirely of $CaSO_4$ and showed no trace of chrome. It is assumed that either the SO_4 ions of the outer sphere enter into reaction or there is initially the expulsion of SO_4 ions from the inner sphere by the stronger complex formers such as $HCOO$, and then all the SO_4 ions react with the ions of the alkali earth metals. Special investigation is necessary to determine which of these is true.

Dry Tanning of Russian Leather. By M. R. Litvinov and S. D. Kovtunovick. *Legkaya Prom.* **9,** No. 5, 10 (1949). Through *Chem. Abst.* **47**, 1960 (1953). The drum is charged with extract (9-10 percent by weight of split but unlimed hide, Na_2SO_3 (5-6 percent by weight of extract), and water to give a density of 10.5-11°Be, thoroughly mixed, and heated, if necessary; pH of the liquor must be approximately equal to 5.5; initial temperature is raised to 20°; and liquid coefficient is 0.7-1.0. Chromed hide is then tanned in 24 hours, with final temperature of liquors 30°. Utilization of tannins is 95.5-96.0 percent; coefficient of tanning is 25-28 after 6 hours, with 32-36 for finished leather. Tannin consumption is 44.45 kg. per 100 square meters of finished leather.

Fermentative Softening Instead of Pickling. By K. A. Krasnov. *Legkaya Prom.* **9,** No. 4, 19 (1949). Through *Chem. Abst.* **47,** 1960 (1953). By reducing the acid content of pickle, its bacteriocidal action is lowered and the pickle becomes, in the final analysis a weak acid solution. This creates sufficiently favorable conditions for the development of certain types of microorganisms. These microorganisms secrete different enzymes, in particular proteolytic, which soften the collagen fibers. Sheepskins were softened by creating conditions for the development of acidophilic microflora (which are always present in the hide). Results were satisfactory.

Influence of Chrome Reducers on Leather Characteristics. By I. P. Strakhov. *Legkaya Prom.* **9,** No. 3, 14 (1949). Through *Chem. Abst.* **47,** 1960 (1953). Dichromate was reduced with sulfite cellulose extract, pine sawdust, cotton combings, sulfur dioxide, glucose, and tanning fluid. Complex Cr ions were charged differently; glucose Cr solution contained mostly positive ions, while others contained only or mostly negative ions. After tanning, spent liquor was analyzed for Cr_2O_3 content basicity, and charge of complex ions. Electrophoretic tests indicated change in the charge of complex ions. Movement in all cases was toward the anode only, indicating negative charge even after 6 hours tanning and regardless of initial charge. Specimens tanned with glucose chrome liquor contained somewhat less chrome than those tanned with liquors which were reduced with SO_2 and pine sawdust, and the same amount of chrome as leather tanned with chrome reduced by sulfite cellulose extract. Specimens tanned with glucose reduced liquor had a higher shrinkage temperature and smaller percentage of contraction.

Reducing the Ash Content of Syntan AN. By A. I. Smetkin. *Legkaya Prom.* **9,** No. 6, 26 (1949. Through *Chem. Abst.* **47,** 1960 (1953). Consumption of H_2SO_4 for sulfonation of crude anthracene to make Syntan AN is reduced close to the theoretical by blowing hot dry air continuously through the sulfonic mass at 115°-120°. Ash content was reduced from 63.1 to 36.1 percent.

Shrinkage of Leather at High Temperatures. By N. I. Egarkin. *Legkaya Prom.* **9,** No 3, 12 (1949). Through *Chem. Abst.* **47,** 1960 (1953). An autoclave was used in the determination of shrinkage temperature. Leather strips of known moisture content were used, and temperature was raised until the strips showed evident signs of shrinkage. Water content of the strips was determined before and after the tests. When the moisture content was reduced to 25-30 percent shrinkage temperature remained unchanged, but after that, it rose with decreasing moisture content. At a moisture content of 7-8 percent, the leather was resistant against heat up to 170°.

High Dispersion Clays as Leather Fillers. By M. P. Zhurbenko, R. V. Rykberg, and S. V. Gerasev. *Legkaya Prom.* **9,** No. 4, 15 (1953). Through *Chem. Abst.* **47,** 1960 (1953). Clays capable of forming highly dispersed suspensions in water can be used as fillers for sole and insole leathers. The clay is bonded more firmly with the leather fibers than are glucose and salts. Filling with clay raises considerably the coefficient of tanning.

Oxidation-Reduction Properties of Solutions Used in Treating Fur Skins. By I. P. Stefanovich. *Legkaya Prom.* **9,** No. 12, 28 (1949). Through *Chem. Abst.* **47,** 2523 (1953). The determination of oxidation-reduction potentials during treatment of furs with oxidizable dye intermediates is said to be advantageous.

Interaction of Alkali with Wool and Skin of Pelt. By K. A. Krasnov. *Legkaya Prom.* **9,** No. 10, 28 (1949). Through *Chem. Abst.* **47,** 2523 (1953). During the same time interval, not exceeding one hour, skin absorbs 1.5 times as much alkali as wool. In sodium carbonate solutions, containing 2 grams of carbonate per liter, wool reaches equilibrium with the solution in 45 minutes while the skin does not reach equilibrium in 90 minutes. After 60 minutes, skin gives up a portion of the alkali to the solution while wool continues absorption. Absorption of alkali by albumins increases with concentration of the solution but is not proportional to the concentration. Immediately after washing, the wool and skin were degreased in alkali-soap solution; both absorbed an additional amount of alkali from this solution. The more concentrated the solution in the wash tank, the less the absorption of alkali from the degreasing tank. In the degreasing tank, skin absorbed alkali in proportion to rise of total alkalinity, showing no apparent signs of saturation as total alkali increased from 3.0 to 5.18 grams per liter; wool showed signs of saturation even at 3.07 grams per liter. When degreased wool and skins were washed in weakly alkaline solutions, both gave up 20-23 percent of alkali to the solution, establishing a new equilibrium after one-half hour.

Improving the Quality of Spruce Extract. By O. S. Apenaev. *Legkaya Prom.* **9,** No. 11, 21 (1949). Through *Chem. Abst.* **47,** 1953 (1953). Prior to hot extraction, the ground bark is treated with cold water to remove nontanning substances. Nontannins removed are almost three times as great as the loss of tannins.

Albumin Composition of Hide. By N. V. Chernov and V. E. Kotina. *Legkaya Prom.* **9,** No. 11, 21 (1949). Through *Chem. Abst.* **47,** 2525 (1953). Soluble albumins of hide were separated by existing methods which were improved by use of the Voisene reaction to determine time for change of liquids and by precipitation of nitrogenous material of the extracts by heating in acid medium, with $Cu(OH)_2$ and with tannin. Despite different methods of treatment, practically the same amount of nitrogenous material was removed in all cases. The epidermis does not contain albuminous substances soluble in alkali and insoluble in salt solution; such substances are contained only in the corium.

A Rapid Determination of Water Content in Tannery Products by the K. Fischer Method. By R. Allegrini. *Cuoio, Pelli, Mat. Concianti* **28,** 409 (1952). Through *Chem. Abst.* **47,** 2525 (1953). The microanalytical method of K. Fischer can be applied to tanning extracts, fats, bating materials, salts and leather. The method is very rapid and gives good agreement with the direct water determinations except in the cases of products containing reducing substances such as cold-soluble quebracho extracts. Results are tabulated.

The Use of Synthetic Tannins, Particularly in Mixtures with Chestnut Extract. By M. Asch. *Cuoio, Pelli, Mat. Concianti* **28,** 400 (1952). Through *Chem. Abst.* **47,** 2525 (1953). The addition of syntans to natural and sweetened chestnut wood extracts decreases the content of insoluble matters and lightens the color of both the extracts and the leather.

Leather and Tanning Agents V. The Macromolecular Theory of Tanning. By H. Batzer. *Chem. Zeit.* **76,** 397 (1952). Through *Chem. Abst.* **47,** 2525 (1953). A polyamide (Ultramid 6A) was used as a model substance for hide. Both were found to bind almost equal parts of quebracho tannin per unit of nitrogen present. The same was true of phenol and pyrocatechol, except that they were easily washed out of the polyamide with water. Collagen, elastin, and polyamide fibers were tanned with quebracho, then detanned by treatment with nitrous acid, neutralization, and washing with water. The behavior of fresh, tanned, and detanned fibers was compared under polarized light and during reversible extension. Tanning changed the properties, and detanning restored them to the original. It was concluded that tanning is not due to cross-linking, but to binding by secondary valence forces or hydrogen bridges. This binding displaces water from the hide, making it more resistant to hydrolysis and fermentation. The second function of tanning is "softening". Any material which dehydrates and softens hide should produce leather. This was tested by impregnating hide with monomers and polymerizing *in situ*. Styrene, vinyl acetate, or methyl methacrylate treatment showed a dehydrating, but not a softening, action. Copolymerization with vinyl ethers gave leather like products, which were further improved by the incorporation of maleic anhydride. It was shown that true copolymers of relatively high molecular weight had been formed. The products compared favorably with leather, especially in impermeability to water.

Colored Sarsaparilli *(Muehlenbeckia sagittifolia).* Characterization and Determination of Its Tanning Matter. By E. Sedelli. *Rev. Fac. Cienc. Quim. Univ. Nacl. La Plata* **24,** 135 (1952). Through *Chem. Abst.* **47,** 2525 (1953). Analytical data are given for stalks of *M.sagittifolia*, determined by the official methods of tannin analysis. About 4.6 percent of tannin can be extracted by this method. The tannin is of the catechol type.

Interaction of Chrome and Sulfite Cellulose Liquors During Combination Tannage. By L. P. Gaidarov. *Legkaya Prom.* **9,** No. 7, 18 (1949). Through *Chem. Abst.* **47,** 2525 (1953). Electrophoretic observations indicate that in mixed chrome and lignosulfonate liquors the chrome complex in general is not negatively charged; this also confirms the absence of substantial changes in its inner sphere. Electrolysis of the mixed liquors showed an independent movement to the electrodes of the positively charged chrome complexes and lignosulfonate anions, indicating absence of coordinative bonds between the lignosulfonate tannins and the chrome complexes. Spectrophotometric observations confirm that addition of lignosulfonate causes no substantial changes. The absorption curves and magnitude of optical density of mixed liquors are additive.

Leather. II. Reaction Mechanism of Oil Tanning. By Y. Inone, and R. Kawamura. *J. Agr. Chem. Soc. Japan* **22,** 67 (1948). Through *Chem. Abst.* **47,** 2526 (1953). Oil Tanning by the wet method was applied to raw skins. Horse or rabbit skin (40 g.) was pretreated by one of the following processes: (a) liming; (b) liming followed by

deliming with NH_4Cl; (c) as in (b) followed by pickling. The skin was then treated with cod liver oil 400, H_2O 100, and reduced Fe 0.6 g. for 4 weeks on a horizontal shaker at room temperature. A control test was run with glass fiber tape instead of raw skin. Peroxide value was determined after 1, 2, 3, and 3.5 weeks, and heat stability of the treated skins was observed.

III, Ibid 22, 68 (1948). The glycerine-aldehyde value of Schibstad was determined.

IV. Ibid 22, 69 (1948). The acid value was determined. When the skin was well tanned, as judged from shrinkage and gelatinization temperatures, the peroxide value was lower than the control. The glyceride-aldehyde value increased and then decreased, and the acid value increased only slightly. The mechanism of oil tannage is considered to be the accumulation of peroxides owing to the oxidation of oil followed by the formation of glyceride-aldehyde, which is the important factor in tanning. Skin pretreated with lime only gave the best results.

Variation of the pH of Tanning Solutions of Sulfotans. By G. I. Kutyanin. *Legkaya Prom.* **9,** No. 8, 27 (1949). Through *Chem. Abst.* **47,** 2526 (1953). A sharp increase of pH value of sulfosyntans was observed during tanning. A mechanism of OH accumulation is suggested.

Effect of Water Solubles on Thermal Stability of Leather. By L. P. Gaidarov and S. V. Pastukhova. *Legkaya Prom.* **9,** No. 10, 23 (1949). Through *Chem. Abst.* **47,** 2526 (1953). In treating leather strips with water, there was considerable removal of water solubles, accompanied by a rise of shrinkage temperature. The effect indicates that water solubles do not form bridges between the polypeptide chains, which could make the structure more resistant to heat. Possibly removal of water solubles restores the hydrogen bond between adjacent peptide groups, with resultant strengthening of the structure.

The Dyeing and Tanning Matters of Young Fustic of the Venezia Giulia. By L. Ferro. *Cuoio, Pelli, Mat. Concianti* **28,** 316 (1952). Through *Chem. Abst.* **47,** 2526 (1953). The powdered extract of the wood *Rhus cotinus* (analysis by filter method) gives: tannins 44.3, nontannins 44.8, insolubles 1.2, moisture 9.7, ash 9.39 percent, pH 5.15. The tannin is a mixture of catechol (40%) and pyrogallol tannins. Some experiments are described of tanning sheep and goat skins, and of dyeing rayon and cotton fabrics with basic colors.

Proposition of Standards for Leather for Civil Purposes. By E. Simoncini. *Cuoio, Pelli, Mat. Concianti* **28,** 316 (1952). Through *Chem. Abst.* **47,** 2526 (1953). The following standards are proposed: $H_2O \leqq 15\%$; ash $\geqq 1.75\%$; fat $\geqq 2.5\%$; organic soluble matter $\leqq 13\%$; leather substance $\leqq 66.5\%$ tannage index $\leqq 85$; apparent density $\leqq 0.925$; strength $\leqq 2.6$ kg. per sq. mm. of section; stretch $\leqq 25\%$; H_2O absorption $\leqq 18\%$; shrinkage temperature $\leqq 72°$. Methods for these determinations are given.

Heat Denatured Gelatin. By L. F. Tice and A. W. Moore. *J. Am. Pharm. Assoc.* **41,** 631 (1952). Through *Chem. Abst.* **47,** 2526 (1953). Gelatins from both acid-and alkali-treated precursors are denatured when subjected to dry heat at 120, 150, and 170°. The changes produced are progressive, passing from an altered solubility and swelling in H_2O to that state in which pepsin and papain are not able to effect complete hydrolysis. The higher the temperature the shorter the time required. The denaturation is not due to dehydration per se because no such property changes are produced by complete desiccation *in vacuo* over Dehydrite.

Two-Dimensional Chromatography of Amino Acids on Buffered Papers. By A. L. Levy and D. Chung. *Anal. Chem.* **25,** 396 (1953). Previous systems for two-dimensional chromatography of amino acids—for example, collidine-phenol-0.3 percent ammonia—were not completely satisfactory owing among other things, to irregularly shaped spots, lack of reproducibility, incomplete separation, discoloration of the paper, and unpleasant odor. The solvent system 4:1:5 butanol-acetic acid - water - 1:1 M-cresol-phenol, ph 9.3 borate buffer, overcomes these difficulties, allowing completion of the chromatogram in 40 hours. Method of conducting test are described in detail. Photographs of chromatograms are given.

Nylon-Coated Leather. By F. Leonard, T. B. Blevins, W. S. Wright, and M. G. DeFries. *Ind. Eng. Chem.* **45,** 773 (1953). Since leather is used extensively in fabricating prostheses and, since the leather is usually worn in direct contact with the skin where it is subject to acid and alkaline sweat and bacterial skin flora, some method of protecting the leather was considered essential. Nylon FM-6501, manufactured by DuPont, was selected as the plastic most likely to answer all of the requirements for the protective coating material for the leather. The nylon was dissolved in 2-propanol-water at 170°F. with stirring, and the leather given 5 coats at 5 minute intervals. A transparent coating of approximately 0.008 inch was obtained. Thereafter the sample of nylon coated leather was subjected to tests involving abrasion resistance, flexure, simultaneous flexing and abrading in synthetic sweat, resistance to synthetic sweat, stress-strain property measurements, and water vapor permeability. Simultaneous tests were conducted on uncoated leather. Comparative values from the tests are given, and these show to the advantage of the nylon coated leather. In addition, field tests by 50 amputees clearly confirm the laboratory tests.

Partition Mechanism of Paper Chromatography. By D. P. Burma. *Anal. Chem.* **25,** 549 (1953). The author attempts to throw more light on the role of cellulose in paper chromatography. In the chromatographic separation on paper, the primary purposes responsible for the separation is undoubtedly partition, but attention is called to the role of absorption which, though a secondary one, cannot be neglected.

Determination of Particle Size Distributions by a Sedimentation Method. By J. S. Smith and R. Gardenier. *Anal. Chem.* **25,** 577 (1953). A simple apparatus for the determination of particle size distributions as functions of Stokes diameter in liquid media is described. A scheme is presented for computing results in such a way that it is not necessary to use Oden's tangential intercept method in routine analyses. The distributions are described in terms of their mean Stokes diameter and second moments about the mean.

Identification of Organic Acids by Circular Paper Chromatography. By J. W. Airan, G. V. Joski, J. Barnabas, and R. W. P. Master. *Anal Chem.* **25,** 659 (1953). The authors describe a somewhat more direct and more rapid chromatographic method for identifying tartaric, citric, malic, malonic, and succinic acids, and mixtures of these.

The Bark-Ross Tannin Problem. By O. Gerngross and E. Gulbaran. *Das Leder* **3,** 205 (1952). The morphological and functional differences between inner bark and outer bark (ross) and the formation of dead ross tissue from living inner bark tissue in the pine family are explained. Sulfite extractions were made of the ross of 4 species of pine. The phlobaphene number, Q, was determined as water soluble tannin plus phlobaphene divided by soluble tannin. It decreases as soluble matter increases. Sulfite extraction after water extraction removed much less additional tannin (from 0.6 to 3.5%) than direct sulfite extraction of the original ross. The following data were obtained: Sulfite extraction was with 2.5 percent each of sodium sulfite and sodium bisulfite on the bark weight.

Species of Pinus	*Water extraction*		*Sulfite extraction*	
	tannin	nontannin	tannin	nontannin
	%	%	%	%
P. brutia	19.9	10.3	23.8	16.4
P. brutia	20.0	9.1	24.6	15.9
P. pinea	11.2	4.0	19.9	11.5
P. silvestris	7.2	4.9	16.6	12.3
P. nigra	4.1	3.9	10.0	10.6

I. D. C.

The Fastness Requirements of Aniline Dyed Leather. By E. Lüscher. *Oesterreichische Leder-Zeitung* **7,** 270 (1952). Leather for clothing, gloves, luggage, etc., should be fast to rubbing and to light. Committees in Germany, England and America are developing methods for testing for fastness. I. D. C.

Wetting Agents in the Leather Industry. By J. A. Sagoschen. *Oesterreichische Leder-Zeitung* **8,** 23 (1953). If properly used, wetting agents can lighten the work and improve leather quality more than any other tanning aid. The agent may be added at any stage, such as to the soak, lime, bate or tan liquors or to the oil or fat liquor, but as a rule, should not be added at more than one stage. The effect of the agent carries over, for example from the soaking to the liming and tanning stages. Addition at several stages would result in very open leather. Adding 1% of a wetting agent to the soak and lime liquors and during oiling (total 3%) is more effective than even 5% added to the soak liquor alone. I. D. C.

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